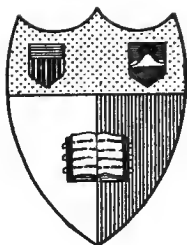


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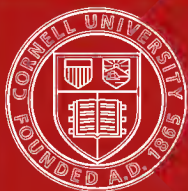
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A MANUAL  
OF  
QUALITATIVE ANALYSIS.

BY  
ROBERT GALLOWAY, F.C.S.,  
PROFESSOR OF APPLIED CHEMISTRY IN THE ROYAL COLLEGE OF SCIENCE FOR  
IRELAND, AUTHOR OF "THE SECOND STEP IN CHEMISTRY," "THE  
FIRST STEP IN CHEMISTRY," ETC.

FROM THE  
FIFTH REWRITTEN AND ENLARGED LONDON EDITION.

WITH ILLUSTRATIONS.



PHILADELPHIA:  
HENRY C. LEA.  
1872.

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## PREFACE TO THE FIFTH EDITION.

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THIS Edition contains numerous and important additions, and some alterations have been made in the arrangement of the different divisions of the book; but the plan or scheme of analysis which formed the foundation of the First Edition, and which is explained in the Preface to the Second and in the Introduction to the present one, remains unchanged, and is the foundation of the present as it was of all the previous Editions. I have continued it, not simply because other teachers, as well as myself, prefer it to the system of Fresenius or that of the Giessen outlines, having found it more successful, especially with students who can only devote a portion of their time to the study of analytical chemistry, but because I believe it to be in accordance with the laws of thought. (1) It exhibits a like progression to the mind; it begins with a few subjects and successively adds to them until the entire system is reached; it proceeds, in short, from the simple to the complex. (2) The Tables are not constructed on the bad system of the Giessen outlines and some other analytical works, or on the system of Fresenius, which is quite as faulty, and still more unpractical for the learner—of *telling* this and *showing* that, making the learner a mere recipient—but on the better system of making the

student *compare, distinguish, judge*; so that thus, instead of being a recipient, he may become an intelligent and active discoverer. In addition to the methods developed in the Tables for separating the members of the different groups, others are given to this Edition which the student ought to practise as soon as he can examine substances correctly by the methods given in the Tables.

The old system of teaching Practical Chemistry had some advantages over the method now generally in use. I have endeavored in the present Edition to remove the defects of the present system by describing very fully the properties of the metals, their oxides and chief salts, in order that the student may carry on with the study of analysis other experimental inquiries, either by preparing substances or by studying other than the analytical properties of bodies.

I have given at the end of each group and important division of the book a series of examination questions in Practical Chemistry; many of them, so far as I am aware, are of an *entirely new character*, and these have been framed, not for testing the memory, which is the only faculty of the mind exercised by the questions usually given at chemical examinations, but for ascertaining whether the student has so studied the science that he is capable of reasoning upon it. Owing to memory-questions forming the bulk of the questions usually given at chemical examinations, it has become no uncommon practice with those who are going in for examination, to commit to memory some one of the smaller text-books on the science, or the pet subjects of the examiner. As the new class of questions I have given cannot be answered by the cram-



ming process, I believe they will ultimately be as generally adopted as what are termed the "arithmetical questions," which I was the first to introduce in my "First Step in Chemistry."

In the portion of the work more immediately devoted to analysis, the following are *some of the additions* which have been made: 1st. Bunsen's flame reactions have been given, with figures of the apparatus. 2d. The detection of the poisonous metals and acid-radicals in the presence of organic matter. 3d. Additional tests for the detection of the individual alkaloids, and more complete systematic methods for the detection of these bodies.

The new notation has been adopted; and the division of the book into three chief parts, and the arrangement of these parts, will, I hope, be found an improvement.

In conclusion, allow me to direct the student's attention to the following extract from Thomas Carlyle's "Address to the Students of the University of Edinburgh:" "By diligence I mean among other things—and very chiefly—honesty in all your inquiries. Pursue your studies in the way your conscience calls honest. More and more endeavor to do that. Keep, I mean to say, an accurate separation of what you have really come to know in your own minds, and what is still unknown. Be careful not to stamp a thing as known when you do not yet know it. Count a thing known only when it is stamped on your mind, so that you may survey it on all sides with intelligence. There is such a thing as a man endeavoring to persuade himself, and endeavoring to persuade others, that he knows about things when he does not know more than the outside skin of them, and he goes flourishing about

with them. There is also a process called cramming in some universities—that is, getting up such points of things as the examiner is likely to put questions about. Avoid all that; it is entirely unworthy of an honorable habit. Gradually see what kind of work you can do; for it is the first of all problems for a man to find out what kind of work he is to do in this universe. In fact, morality as regards study is, as in all other things, the primary consideration, and overrides all others. A dishonest man cannot do anything real. . . . He does nothing but darken counsel by the words he utters.”

ROBERT GALLOWAY.

*December, 1869.*

## PREFACE TO THE SECOND EDITION.

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IN issuing a New Edition of this Manual, I will here briefly describe the scheme or plan of analysis developed in the work, and the way in which the book ought to be used.

In all other works on Qualitative Analysis with which I am acquainted, the properties of the bases and acids, and the application of these properties to the analysis of substances, are treated separately. As a consequence, the student, when he goes through the experiments on each base and acid, performs these illustrations of the properties without perceiving their use or application. In the part of the Work devoted to the analytical course, he is *told what to do* either by tables (as in the "Giessen Outlines," and some other works), or, as in Fresenius, by a more tedious, and, in my opinion, as defective a method. The principles upon which these instructions are based are not given with the instructions, but in a separate chapter of the Work; and unless the student is able himself to unite the two—the principles with the practical instruction—he

becomes a mere analytical machine. Students who can give their whole time and attention to the study of the science can, if they will, accomplish this; but I have found by experience that those who can only devote some five or six hours in the week to the acquirement of the science fail to become intelligent analysts by this system.

The system is very difficult, as well as defective; it is so difficult that those who employ it generally teach one thing, useless in itself, in order that they may teach another; they teach the student first to look for one acid and one base—a limitation which is not adopted in actual practice—solely for the purpose of rendering the course in which they have to look for all the bases and acids less difficult.

In the plan I have adopted the properties of the different members of each group are contrasted by placing them in parallel columns; the advantage of this is, that the student, after he has performed the experiments, is able himself to devise methods for the detection and separation of the different members; it places him, in fact, in the position of a judge who has to decide some cause after having heard all the pleadings. It enables him also to judge for himself how many different methods might be adopted in the separation of substances; it therefore enlarges his views, and enables him to *reason* on the methods he adopts.

This Manual is intended to be used in the following way: The student commences with the first group; and after he has performed all the experiments given in the table of that group, several analyses are given him, each of which he examines for the members of this group. When he can perform these practical exercises correctly, he commences the second group—first performing the experiments in the group, and then analyzing several solutions for the members of this group. When he can perform these correctly, he examines several solutions for the members of the first and second groups. In this progressive way he passes through the groups; so that by the time he has completed them he will have become an accurate analyst.

In the former Edition I proposed, and partially carried out, the division of the third group of bases, by employing ammonia as a group reagent; this alteration not only simplifies the subject, but it makes the plan of analysis taught in the laboratory more consonant with the methods adopted in actual practice. This alteration is fully carried out in this Edition, and a more complete description of the properties of the basic groups is given. I have also given in this Edition an outline of the special tests to be adopted in the detection of the acids, and considerable additions have been made in the chapter on the Preliminary Examination of Solids. I have also introduced a

new feature at the very commencement of the book; a series of experimental exercises are given, illustrating the principles upon which analytical operations are based, which it is intended the student should perform before he commences the groups. My aim in writing the book has been to furnish a suitable guide to the beginner; and I confidently hope that this Edition will be found superior to the former in this respect, and that it is what I wish it to be—a Student's Book.

R. G.

DUBLIN, *Nov.* 1857.



# CONTENTS.

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## PART I.

	PAGE
PRELIMINARY REMARKS . . . . .	25
HOW THE BOOK OUGHT TO BE STUDIED . . . . .	27
SOURCES OF ERROR . . . . .	29
ARRANGEMENTS OF THE RESULTS OF AN ANALYSIS . . . . .	30
FIRST BASIC GROUP.—Potassic, sodic, ammoniac, and lithic oxides	33
TABLE I.—Behavior of the members of the group with the special reagents . . . . .	34
Precautions to be attended to in the analysis of this group .	36
Properties of the metals, the oxides, the sulphides, the chlorides, the nitrates, the sulphates, of this group . . . . .	37
General characters of the salts of this group . . . . .	41
Remarks on the individual members of the group, with additional special tests . . . . .	41
Exercises on this group . . . . .	46
SECOND BASIC GROUP.—Baric, strontic, calcic, and magnesian oxides . . . . .	47
TABLE II.—Behavior of the members of the first division of the second group with the special reagents . . . . .	49
Precautions to be attended to in the analysis of this group .	51
Properties of the metals, the oxides, the sulphides, the chlorides, the nitrates, the sulphates, of this group . . . . .	51
General characters of the salts of this group . . . . .	54
Remarks on the individual members of the group, with additional special tests . . . . .	55
Exercises on this group . . . . .	59

THIRD BASIC GROUP.—Zincic, manganous, nickelous, and cobaltous oxides . . . . .	61
TABLE III.—Behavior of the third group with the special reagents . . . . .	62
Precautions to be attended to in the analysis of this group .	64
Properties of the metals, the oxides, the sulphides, the chlorides, the nitrates, the sulphates, of this group . . . .	65
General characters of the salts of this group . . . . .	68
Remarks on the individual members of the group, with additional special tests . . . . .	69
Exercises on this group . . . . .	74
FOURTH BASIC GROUP.—Aluminic, chromic, ferric, ferrous oxides; aluminic, chromic, and iron phosphates; the phosphates of the alkaline earths, baric, strontic and calcic oxalates; uranic and titanlic oxides . . . . .	76
TABLE IV.—Behavior of the fourth group with the special reagents . . . . .	78
Properties of the metals, the oxides, the sulphides, the chlorides, the nitrates, the sulphates, of this group. . . .	79
General character of the salts of this group . . . . .	83
Remarks on the individual members of the group, with additional special tests . . . . .	84
Exercises on this group . . . . .	88
PROPERTIES OF THE PHOSPHATES AND OXALATES OF THE GROUP .	90
TABLE V.—Method for separating these phosphates and oxalates . . . . .	93
Precautions to be attended to in their analysis . . . .	92
Other methods for the separation of these phosphates and oxalates, and other members of the group . . . . .	94
Exercises on the phosphates and oxalates . . . . .	96
Properties of uranic oxide . . . . .	97
“ of titanlic oxide . . . . .	97
FIFTH BASIC GROUP.—Auric, platinic, stannous, stannic, antimonious oxides; arsenious and arsenic anhydrides . .	99
METHODS FOR THE EXAMINATION OF THE GROUP . . . . .	100
Properties of the metals, the oxides, the sulphides, the chlorides, and the hydrides, of As and Sb . . . . .	102
General characters of the salts of this group . . . . .	112

Remarks on the individual members, with their special tests . . . . .	115
Exercises on this group . . . . .	134
SIXTH BASIC GROUP.—Argentio, mercurous, mercuric, plumbic, bismuthous, cupric, and cadmic oxides . . . . .	136
TABLE VI.—Behavior of the sixth group with the special reagents . . . . .	138
Precautions to be attended to in the analysis of the group . . . . .	140
Properties of the metals, the oxides, the sulphides, the chlorides, the nitrates, the sulphates, of the group . . . . .	142
Remarks on the individual members of the group, with additional special tests . . . . .	147
Exercises on this group . . . . .	160
GENERAL PROPERTIES OF THE DIFFERENT BASIC GROUPS . . . . .	163
TABLE VII.—Behavior of the basic groups with the general reagents . . . . .	166
Precautions to be observed in examining for the basic groups . . . . .	171
Exercises on the basic groups . . . . .	174
CLASSIFICATION OF THE ACIDS . . . . .	175
INORGANIC ACIDS . . . . .	176
Behavior of the inorganic acids and their radicals with reagents . . . . .	176
Chromic acid . . . . .	176
Sulphuric acid . . . . .	178
Sulphurous acid . . . . .	179
Hyposulphurous acid . . . . .	180
Boracic acid . . . . .	180
Orthophosphoric acid . . . . .	182
Pyrophosphoric acid . . . . .	185
Metaphosphoric acid . . . . .	185
Carbonic acid . . . . .	185
Oxalic acid . . . . .	187
Silicic acid . . . . .	188
Hydrofluoric acid . . . . .	191
Hydrosulphuric acid . . . . .	193
Hydrochloric acid . . . . .	194
Hydriodic acid . . . . .	195
Iodic acid . . . . .	197
Hydrobromic acid . . . . .	198
Hydrocyanic acid . . . . .	200
Nitric acid . . . . .	203
Nitrous acid . . . . .	206

	PAGE
Chloric acid . . . . .	206
CLASSIFICATION OF THE INORGANIC ACIDS, INCLUDING OXALIC ACID . . . . .	208
GENERAL PROPERTIES OF THE INORGANIC ACIDS . . . . .	208
CHARACTERISTIC TESTS FOR THE INORGANIC ACIDS . . . . .	211
PREPARATION OF THE SUBSTANCES FOR THE EXAMINATION OF THE ACIDS, AND THE METHODS TO BE FOLLOWED IN THE EXAMINATION . . . . .	212
PRELIMINARY EXAMINATION FOR THE INORGANIC ACIDS . . . . .	214
Exercises on the inorganic acids . . . . .	215
ORGANIC ACIDS . . . . .	216
BEHAVIOR OF THE ORGANIC ACIDS AND THEIR RADICALS WITH REAGENTS . . . . .	217
Tartaric acid . . . . .	217
Citric acid . . . . .	219
Malic acid . . . . .	221
Benzoic acid . . . . .	222
Succinic acid . . . . .	222
Tannic acid . . . . .	223
Gallic acid . . . . .	224
Acetic acid . . . . .	224
Formic acid . . . . .	226
Uric acid . . . . .	227
CLASSIFICATION OF THE ORGANIC ACIDS . . . . .	228
GENERAL PROPERTIES OF THE ORGANIC ACIDS . . . . .	228
CHARACTERISTIC TESTS FOR THE ORGANIC ACIDS . . . . .	229
PREPARATION OF THE SUBSTANCES FOR THE EXAMINATION OF THE ACIDS, AND THE METHODS TO BE FOLLOWED IN THE EXAMINATION . . . . .	230
PRELIMINARY EXAMINATION FOR ORGANIC ACIDS . . . . .	231
Exercises on the organic acids . . . . .	232
EXAMINATION OF LIQUIDS AND SOLIDS . . . . .	233
PRELIMINARY EXAMINATION OF A LIQUID . . . . .	233
Exercises . . . . .	236
PRELIMINARY EXAMINATION OF SOLIDS . . . . .	236
CLASSIFICATION OF SOLIDS . . . . .	236
COLORATION OF THE GAS FLAME BY SOLIDS . . . . .	237

TABLE VIII.—Examination of a solid in a glass tube closed at one end . . . . .	242
Examination of a solid in an open tube . . . . .	247
TABLE IX.—Examination of a solid on charcoal . . . . .	250
TABLE X.—Examination of a solid with cobaltic nitrate, with sodic carbonate, and with borax . . . . .	251
Fusibility of minerals . . . . .	255
TABLE OF VOLATILE ELEMENTS WHICH CAN BE REDUCED AS FILMS . . . . .	258
SOLUTION OF A SOLID WHICH IS NEITHER A PURE METAL NOR AN ALLOY, AND IS DESTITUTE OF ORGANIC MATTER . . . . .	261
TREATMENT AND SOLUTION OF A SOLID WHICH IS NEITHER A PURE METAL NOR AN ALLOY, AND WHICH CONTAINS ORGANIC MATTER . . . . .	264
SOLUTION OF A PURE METAL OR AN ALLOY . . . . .	267
Exercises . . . . .	268

## PART II.

## ANALYSIS OF ORGANIC SUBSTANCES.

PRELIMINARY REMARKS . . . . .	269
ELEMENTARY ANALYSIS . . . . .	270
Test of an organic compound . . . . .	270
Tests for nitrogen . . . . .	270
“ sulphur . . . . .	271
“ phosphorus . . . . .	272
“ inorganic substances . . . . .	272
PROXIMATE ANALYSIS OF ORGANIC SUBSTANCES . . . . .	272
Analysis of the inorganic portion of organic substances . . . . .	273
Animal chemistry . . . . .	277
ALBUMINOID GROUP, ITS PROPERTIES . . . . .	278
Properties and reactions of albumen . . . . .	282
“ “ fibrin . . . . .	286
“ “ casein . . . . .	288
“ “ globulin . . . . .	289
Recapitulation and remarks on the group . . . . .	290
GELATINOUS GROUP, ITS PROPERTIES . . . . .	291
Properties and reactions of gelatine . . . . .	292
“ “ chondrin . . . . .	293

	PAGE
SACCHARINE GROUP . . . . .	294
Properties and reactions of milk sugar . . . . .	295
"        "        glucose . . . . .	295
"        "        inosite . . . . .	297
ORGANIC BASES . . . . .	298
Properties and reactions of urea . . . . .	298
"        "        creatinine . . . . .	300
"        "        creatin . . . . .	301
ORGANIC ACIDS . . . . .	302
Properties and reactions of lactic and sarcolactic acids . . . . .	302
"        "        hippuric acid . . . . .	303
"        "        glycocholic acid . . . . .	304
"        "        glyco-hyocholic acid . . . . .	304
"        "        taurocholalic acid . . . . .	305
"        "        cystine . . . . .	305
"        "        xanthine . . . . .	306
"        "        cholestrin . . . . .	307
COLORING MATTER . . . . .	307
"        "        of the urine . . . . .	307
"        "        "        bile . . . . .	307
"        "        "        blood . . . . .	308
Tests for blood . . . . .	308
"        bile . . . . .	309
METHODS FOR ANALYZING QUALITATIVELY ANIMAL SECRETIONS . . . . .	309
QUALITATIVE ANALYSIS of urine . . . . .	313
"        "        urinary calculi . . . . .	317
PROPERTIES of vegetable albumen . . . . .	320
"        "        fibrine . . . . .	320
"        "        caseine . . . . .	320
THE SACCHARINE GROUP . . . . .	321
Properties of cellulose . . . . .	321
"        starch . . . . .	323
"        gum . . . . .	324
"        cane-sugar . . . . .	325
Exercises . . . . .	326
ORGANIC BASES AND MECONIC ACID . . . . .	327
Properties and reactions of nicotine . . . . .	328
"        "        morphine . . . . .	329
"        "        narcotine . . . . .	332



Properties and reactions of quinine . . . . .	334
“ “ cinchonine . . . . .	336
“ “ strychnine . . . . .	336
“ “ brucine . . . . .	339
“ “ meconic acid . . . . .	340
DETECTION OF OPIUM IN ORGANIC MIXTURES . . . . .	341
METHODS FOR THE DETECTION OF THE POISONOUS ALKALOIDS IN ORGANIC MIXTURES . . . . .	341
Exercises . . . . .	345

## PART III.

OPERATIONS . . . . .	346
Solution . . . . .	346
Precipitation . . . . .	347
Filtration . . . . .	348
Decantation . . . . .	349
Evaporation . . . . .	349
Distillation . . . . .	350
Ignition . . . . .	350
Sublimation . . . . .	350
Fusion . . . . .	350
Deflagration . . . . .	351
The blowpipe . . . . .	351
Blowpipe lamps . . . . .	352
“ supports . . . . .	353
“ apparatus . . . . .	354
Bunsen's gas lamp and the chief divisions of its flame . . . . .	358
The six points in Bunsen's gas lamp flame . . . . .	360
Method of examination in these different points of the flame . . . . .	361
Emission of light by substances . . . . .	363
The melting-point of the flame . . . . .	364
Flame-coloration . . . . .	364
Oxidation and reduction of substances in the gas-flame . . . . .	365
Reduction in glass tubes . . . . .	365
Reduction on splinters of charcoal . . . . .	366
Films upon porcelain . . . . .	367
Examination of the films . . . . .	368
Reactions of the elements in the gas-flame . . . . .	370
Apparatus required in photo-chemical experiments . . . . .	370

	PAGE
REAGENTS . . . . .	373
Hydrochloric acid . . . . .	373
Nitric acid . . . . .	373
Aqua regia . . . . .	373
Sulphuric acid . . . . .	374
Tartaric acid . . . . .	375
Sodic hydric tartrate . . . . .	375
Acetic acid . . . . .	375
Hydrosulphuric acid . . . . .	375
Sulphurous acid and anhydride . . . . .	376
Chlorine-water . . . . .	376
Hydrofluosilicic acid . . . . .	376
Oxalic acid . . . . .	376
Ammonic oxalate . . . . .	376
Ammonia . . . . .	376
Ammonic chloride . . . . .	377
Ammonic sulphide . . . . .	377
Ammonic carbonate . . . . .	377
Ammonic nitrate . . . . .	377
Ammonic arseniate . . . . .	377
Arsenic acid . . . . .	377
Ammonic molybdate . . . . .	377
Potassic sulphate . . . . .	378
Potassic nitrite . . . . .	378
Potassic ferrocyanide . . . . .	378
Potassic ferricyanide . . . . .	378
Ammonic sulphocyanide . . . . .	379
Potassic sulphocyanide . . . . .	379
Potassic chromate . . . . .	379
Potassic cyanide . . . . .	379
Sodic hydrate . . . . .	380
Sodic carbouate . . . . .	380
Disodic hydric phosphate . . . . .	380
Sodic acetate . . . . .	380
Sodic hydric sulphite . . . . .	380
Borax . . . . .	381
Sodic potassic carbonate . . . . .	381
Sodic ammonic hydric phosphate . . . . .	381
Dihydric dipotassic metantimoniate . . . . .	381
Baric-chloride . . . . .	381
Baric-nitrate . . . . .	382

	PAGE
Lime-water . . . . .	382
Calcic chloride . . . . .	382
Calcic sulphate . . . . .	382
Magnesian sulphate . . . . .	382
Baric carbonate . . . . .	382
Ferrous sulphate . . . . .	382
Ferric chloride . . . . .	382
Plumbic acetate . . . . .	382
Mercurous nitrate . . . . .	382
Mercuric chloride . . . . .	383
Cupric sulphate . . . . .	383
Ammonio-sulphate of copper . . . . .	383
Argentio nitrate . . . . .	383
Ammonio-nitrate of silver . . . . .	383
Cobaltic nitrate . . . . .	383
Platinic chloride . . . . .	383
Auric chloride . . . . .	383
Stannous chloride . . . . .	384
Plumbic peroxide . . . . .	384
Copper turnings . . . . .	384
Zinc . . . . .	384
Nessler's test . . . . .	384
Solution of indigo . . . . .	385
Distilled water . . . . .	385
Reagent papers . . . . .	385
Preparation of blue litmus paper . . . . .	385
"    reddened litmus paper . . . . .	385
"    turmeric paper . . . . .	386
Schonbein's test-papers for hydrocyanic acid . . . . .	386
Preparation of Brazil-wood paper . . . . .	386
LIST OF APPARATUS REQUIRED FOR QUALITATIVE ANALYSIS . . . . .	386
APPENDICES . . . . .	387
Appendix A.—Treatment of silver residues . . . . .	387
Appendix B.—Treatment of platinum residues . . . . .	388
Appendix C.—Treatment of gold residues . . . . .	389
INDEX . . . . .	391



# QUALITATIVE ANALYSIS.

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## PART I.

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PRELIMINARY REMARKS, 1. HOW THE BOOK OUGHT TO BE STUDIED, 6. SOURCES OF ERROR, 11. ARRANGEMENT OF THE RESULTS OF AN ANALYSIS, 12.

1. *Preliminary remarks.*—The object of *qualitative* analysis is to ascertain what elements are present, and how they are combined in substances of *unknown composition*. The object of *quantitative* analysis is to determine the quantity of each element present in substances. Hence, qualitative must always precede quantitative analysis, and in numerous cases it is not necessary to make a quantitative investigation, the *quality* of the substance affording all the information that is required. Qualitative and quantitative analysis, forming, therefore, two distinct branches of chemical analysis, are studied separately and independently of each other, and the study of the former, by which the component parts of substances are revealed, naturally precedes that of the latter.

2. The complete aim of qualitative analysis is to discover unknown as well as known bodies in substances, but it will be manifest that a course of qualitative analysis designed to teach students this branch of analytical chemistry must be more restricted; not only must the unknown form no part of the scheme, but those elements and compounds must also be excluded which, from their rarity, or from their having no useful application, are comparatively unimportant. Organic bodies, with the exception of a few of the more commonly occurring organic acids, are also excluded and a student's course is confined, with the exception named, to the inorganic or mineral substances

which are commonly met with in nature, or which have some useful application. A course of this kind is given in Part I. of this book.

3. The methods of qualitative analysis consist in bringing the substance under examination in contact with *other bodies of known properties*, and observing the *phenomena* which ensue. These phenomena consist in alterations of *form or color*, depending upon some *chemical change*; the change of form most frequent is the formation of a *precipitate* which, in many cases, possesses a characteristic color, but sometimes *effervescence* takes place, and sometimes *deflagration*. The *bodies* with which the substance under examination is brought into contact are called *tests or reagents*, and the phenomena produced by their contact with the substance are called *reactions*. Acids, bases, salts, and elements are alike used as reagents, and the methods for preparing them in a state of purity, and the preparation of their solutions, are described in Part III. of the book, along with a description of the principal operations employed in analysis, and a list of the apparatus required. Reagents employed for the detection of individual bodies are called *special reagents*; reagents which are employed to detect groups of substances are called *general or group reagents*. A special reagent is said to be *characteristic* when it produces a reaction so decisive that it admits of no mistake.

4. It has not only to be proved, in complete and accurate analytical investigations, that certain substances are present, but it has also to be proved, which is generally more difficult, that all other bodies but those discovered are absent. This cannot be accomplished by testing indiscriminately and separately for each base and acid radical; it requires, not only that the reagents be added in a certain order, but that the bodies which have to be sought for be separated *first into groups or families*, and afterwards each group divided and subdivided until the presence or absence of each of its members is indubitably established. The separation of bodies into groups is effected by observing some chemical property common to several substances, and peculiar to them, by which means they can be classified into a group, and all other bodies excluded.

5. The analyst, by means of reagents, interrogates the substance to be analyzed as to what are its component parts; the reactions are the language in which the answer is returned. The student has, therefore, to learn the mode

of questioning the substance, and the language in which the answer will be conveyed; in other words, he has to learn, not only what general and special reagents are to be employed, but the order in which they are to be applied, and also, the reactions they produce with the bases and acid radicals, before he can attempt to search for these bodies in substances. No amount of *reading or lecture-hearing* will furnish the student with this knowledge; he can only obtain it by making the experiments himself of the different bases and acid radicals with the reagents, and "*he must always reflect, before the addition of the reagent, for what purpose he applies it, and what are the phenomena he intends to produce,*" and the conditions indispensable for the production of correct and decisive reactions must be carefully observed, for a half knowledge in all departments of science is of little worth, but in chemical analysis it is worse than useless. The phrase "the behavior or deportment of bodies with reagents" is frequently substituted for the term *reactions*.

6. *How the book ought to be studied.*—In the group tables, the behavior of the different members of the group with the special reagents are contrasted by placing them in parallel columns; the student has to perform these experiments, and to note the analogies and differences the members display with the same reagents. The order in which the experiments are to be made will be best explained by the aid of Table I.; the experiments in the paragraphs marked A 1, B 1, and C 1, are first made, and in the order given; then those in A 2, B 2, and C 2; then those in A 3, B 3, and C 3; and, finally, those in A 4, B 4, and C 4. In making the experiments, the conditions which favor or prevent precipitation, together with the appearances of the precipitates, must be carefully noted and remembered, and in all the experiments the *chemical change* must be described, when possible, in the form of a diagram or equation in the student's note-book. The student, after he has made the experiments, will be able of himself to devise methods for the *separation and detection* of the different members; the knowledge he has acquired of the properties of the bodies places him, in fact, in the position of a judge who has to decide some cause, after having heard all the pleadings. He will also be able to decide whether more methods than one could be adopted for the separation of the members by the aid of the reagents given in the table. After he has devised a method for the separa-

tion of the members of a group, he compares it with the one given in the text. He may then proceed to perform the experiments on the different members given under the head of "Remarks on the Individual Members."

7. The student commences with the **FIRST GROUP**, and after he has performed all the experiments as previously described, several solutions are given him, each of which he examines for the members of the group. When he can perform these practical exercises correctly, he proceeds to the **SECOND GROUP**, first performing the experiments and then analyzing several solutions for the members. When he can perform these exercises correctly, he learns by experiment how to separate the two groups by means of Table VII. He then analyzes several solutions for the members of the first and second groups. When he has completed all the basic groups in the manner described, he should analyze about twenty different solutions, and look for all the bases given, after which, the experiments given under the different acids must be performed. The student is then capable of undertaking a complete course of *qualitative analysis*, commencing with substances already in a state of solution, and concluding with the examination of solids.

8. In this edition, the behavior of the bases and acid radicals with a larger number of reagents has been given, and also more methods for the separation of substances. The student ought, after he can analyze solutions for the members of a group by one method correctly, to analyze other solutions of the same group by another method, and so learn all the different methods given for the separation and detection of the different members of any group. He ought, whilst studying each group, to learn to prepare the solutions of the reagents in that group, and also the reagents themselves when methods for their preparation are given in Part III. He ought also to study carefully **THE PROPERTIES OF THE METALS AND THE SALTS**, and it would be well if he were to make some of the experiments there described; answers to the questions given on each group must also be written out.

9. The bases are divided into the following groups:—



## GROUP I.

Potassic Oxide.  
Sodic Oxide.  
Ammonic Oxide.

## GROUP II.

*1st Division.*

Baric Oxide.  
Strontic Oxide.  
Calcic Oxide.

*2d Division.*

Magnesian Oxide.

## GROUP III.

Zincic Oxide.  
Manganous Oxide.  
Nickelous Oxide.  
Cobaltous Oxide.

## GROUP IV.

Aluminic Oxide.  
Chromic Oxide.  
Ferrous Oxide.  
Ferric Oxide.

## GROUP V.

Arsenious Acid.  
Arsenic Acid.  
Antimonous Oxide.  
Stannous Oxide.  
Stannic Oxide.  
Auric Oxide.  
Platanic Oxide.

## GROUP VI.

*1st Division.*

Argentive Oxide.  
Mercurous Oxide.  
Plumbic Oxide.

*2d Division.*

Plumbic Oxide.  
Mercuric Oxide.  
Bismuthous Oxide.  
Cadmic Oxide.  
Cupric Oxide.

10. We may here point out another advantage arising from the separation of substances into groups. It is as easy, for instance, to discover the absence or presence of a group as that of an individual substance; and the absence of a group being proved, it is unnecessary to examine further for any member contained in it.

11. *Sources of error.*—One frequent source of error with the young analyst is the imperfect mixture of the reagents with the solutions to which they are added. Another prolific source of error is the too liberal or the too sparing addition of the reagent, both being objectionable. To show the objectionable nature of a too sparing addition of the reagent, we will suppose the student to be examining a solution for barium and calcium; we will further suppose he has added potassic chromate and obtained a precipitate,\*

\* Whenever a precipitate is obtained, it must be separated from the fluid by *filtration*, if either the fluid or the precipitate has to be examined

which proves the presence of Ba. He filters, and to the filtrate he adds ammoniac oxalate, to test for Ca; he obtains a precipitate with ammoniac oxalate, although Ca is absent, because he has not added a sufficient quantity of the potassic chromate to precipitate all the Ba: thus, by the imperfect addition of a reagent, he arrives at a wrong conclusion. This fruitful source of error, viz., imperfect precipitation, may be avoided by adding to the filtrate a little more of the reagent with which the precipitation was effected. If this produces no further precipitate, the substance has been fully precipitated. Should a further precipitate be produced, it must be removed by filtration before attempting to throw down any other substance. The student must also carefully distinguish between the terms *precipitate* and *filtrate*, and be very particular in thoroughly washing the precipitates which require further examination. The wash-water must not be collected with the filtrate, if this last should be required for further examination. But all these precautions will have been attended to in vain should the experiments be performed in dirty apparatus, this being sufficient of itself to render the results unsatisfactory, if not erroneous.

12. *Arrangement of the results of the analysis.*—The student, during the course of his analytical studies, ought invariably to record the results of each analysis in his notebook, in a systematic and tabular form. An illustration is given to show the method to be pursued.

13. *Preliminary examination of a solid substance.*—1st. It is a colorless, crystallized substance, probably a salt. 2d. Heated alone on charcoal, it deflagrates; a white, infusible substance remaining behind, which becomes luminous, and imparts a crimson color to the flame, probably strontia. 3d. Soluble in water; the solution is neutral to test-paper. As it is soluble in water, a large number of substances, all the insoluble salts, must be absent; as it is neutral to test-paper, all the salts of the alkalies and alkaline earths having an alkaline reaction must be absent; and the soluble salts of the other metals, with the exception of manganese and silver, must be absent, because their soluble neutral salts redden blue litmus paper.

14. The preliminary experiments indicate the presence of strontic nitrate.

further; the fluid for other substances, the precipitate for the detection of the several substances which may have been precipitated, or for the confirmation of any one substance.

15. *Examination of acids and acid radicals.*—The following acids, viz.  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{As}_2\text{O}_3$ ,  $\text{As}_2\text{O}_5$ , and  $\text{CrO}_3$ , were proved to be absent on the examination for the bases.

16. The remainder of the acids, which give precipitates with a baric salt, could not be present; as they likewise form, with strontic salts, insoluble salts.

17. Added to a portion of the original solution  $\text{AgNO}_3$ , no precipitate; absent, Cl, Cy, Br, and I.

18. Added to another portion  $\text{H}_2\text{SO}_4$  and copper turnings, nitrous fumes were evolved, showing the presence of nitric acid.

19. The examination for chloric acid yielded a negative result.

## ACTUAL EXAMINATION.

On the addition of hydrochloric acid, no effervescence; absence of  $\text{CO}_2$  and  $\text{H}_2\text{S}$ .

H Cl.	$\text{H}_2\text{S}$ .	$(\text{NH}_4)_2\text{S}$ .	$(\text{NH}_4)_2\text{CO}_3$	Divided the filtrate into two portions.
No precipitate.	No precipitate.	No precipitate.	A white precipitate formed.	
Absent:	Absent:	Absent:	May be present: $\text{BaCO}_3, \text{SrCO}_3, \text{CaCO}_3$ ; dissolved in $\text{H}^+$ ; divided into two portions.	To one portion added $\text{Na}_2\text{HPO}_4$
$\text{Ag}_2\text{O}$ ,	$\text{Hg O}$ , $\text{Pb O}$ , $\text{Bi}_2\text{O}_3$ , $\text{Cd O}$ , $\text{Cu O}$ ,	$\text{Mn O}$		No precipitate.
$\text{Hg}_2\text{O}$ ,	Absent: $\text{Fe}_2\text{O}_3, \text{Al}_2\text{O}_3$ , and $\text{Cr}_2\text{O}_3$	$\text{Zn O}$		Absent: $\text{Na}_2\text{O}, \text{K}_2\text{O}$ .
and probably	The substance being soluble in water, the phosphates and oxalates of the alkaline earths could not be present.	$\text{Ni O}$		Boiled a portion of the original solution with $\text{NaHO}$ .
$\text{Pb O}$ .	and $\text{As}_2\text{O}_3$ $\text{A}_2\text{O}_5$ $\text{Sn O}$ $\text{Sn O}_2$ $\text{Sb}_2\text{O}_3$ $\text{Pt O}_2$ $\text{Au}_2\text{O}_3$	$\text{Co O}$	To one portion added $\text{CaSO}_4$ Precipitated the Sr from the other portion by $\text{H}_2\text{SO}_4$ .	No ammonia evolved; absence of ammoniacal salts.
			A precipitate, after lapse of sometime. Presence of Sr O, absence of Ba O.	
			No precipitate. Absent: $\text{Ca O}$ .	

20. A few of the rarer elements and compounds have been given, but as they do not form a part of the course, they are not included in the tables; they are distinguished from the more commonly occurring ones by being printed in smaller type.

21. Part II. is intended for advanced students.

## PROPERTIES OF THE BASIC GROUPS.

### FIRST GROUP.

POTASSIC OXIDE ( $K_2O$ ). SODIC OXIDE ( $Na_2O$ ). AMMONIC OXIDE ( $NH_4)_2O$ . LITHIC OXIDE ( $Li_2O$ ).

*Solutions for the reactions.\*—* $KCl$ ,  $NaCl$ ,  $NH_4Cl$ ,  $LiCl$ , *in water.*

22. There are certain names in frequent use for these *oxides*, their *hydrates*, and *salts*, which it is necessary for the student to be familiar with at the very outset. 1st. *Potash*, *soda*, *ammonia*, *lithia*, are names very frequently and indiscriminately employed for these oxides and their hydrates; but the terms *caustic potash*, *caustic soda*, etc., are strictly limited to the hydrates; thus the term *caustic potash* invariably signifies  $KHO$ . 2d. These oxides, and *no others*,† are termed "*the alkalies*;" this term is also indiscriminately employed for the oxides and hydrates; but the term "*the caustic alkalies*" invariably signifies the hydrates. 3d. *Potash*, *soda*, *lithia*, and their salts, are not volatile at a moderate heat, whilst *ammonia* and its salts are volatile; the first three are therefore frequently called the *fixed alkalies*, whilst the fourth is called the *volatile alkali*. 4th. Their salts are termed "*salts of the alkalies*," or "*alkaline salts*," and "*nitrates of the alkalies*," "*alkaline chlorides*," and similar terms are in constant use.

\* At the head of each group will be given the solution of salts which may be employed for the reactions.

† With the exception of two rare ones, viz., *cæsic* and *rubidic oxides*.

TABLE I.

BEHAVIOR OF THE FIRST GROUP WITH THE SPECIAL REAGENTS.

(NH <sub>4</sub> ) <sub>2</sub> O.	K <sub>2</sub> O.	Na <sub>2</sub> O.
A 1. Ammonia and its salts are <i>volatile</i> .	B 1. Potash and its salts are <i>not volatile</i> .	C 1. Soda and its salts are <i>not volatile</i> .
A 2. All ammoniac salts are <i>decomposed</i> with the liberation of free ammonia, when any stronger base, such as CaH <sub>2</sub> O <sub>2</sub> ,* KHO or NaHO, is added to their solutions. If the liquid be gently heated, the ammonia is volatilized, and its presence may then be recognized in three distinct ways. <i>a.</i> By its pungent <i>odor</i> . <i>β.</i> By turning <i>red</i> litmus paper <i>blue</i> . <i>γ.</i> By forming <i>white fumes</i> , when any volatile acid, as HCl, is brought into contact with it.†	B 2. When potassic salts are decomposed by a stronger base, KHO is liberated, but, <i>not being volatile</i> like ammonia, cannot be detected in a similar way.	C 2. When sodic salts are decomposed by a stronger base, NaHO is liberated, but, <i>not being volatile</i> like ammonia, cannot be detected in a similar manner.
A 3. H <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>6</sub> =H <sub>2</sub> T̄, in solution, produces in neutral or alkaline solutions of NH <sub>4</sub> a white crystalline precipitate of NH <sub>4</sub> HC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> =NH <sub>4</sub> HT̄, which is rather more soluble in water than the corresponding potassic salt. Vigorous shaking promotes the formation of this and the corresponding potassic salt.	B 3. H <sub>2</sub> T̄, in solution, throws down from neutral or alkaline solutions of K a white crystalline precipitate of KHT̄. This salt, and the corresponding ammoniac one, are soluble in free alkalies and free mineral acids. Slightly soluble in cold, much more so in hot water. ( <i>Consult par. 44.</i> )	C 3. H <sub>2</sub> T̄, in solution, produces no precipitate in solutions of Na, except in <i>extremely</i> concentrated solutions, NaHT̄ being soluble.
A 4. Ammoniac compounds impart to a lamp flame <i>no</i> characteristic color.	B 4. Potassic compounds tinge the outer lamp flame <i>VIOLET</i> ( <i>Consult par. 46.</i> )	C 4. Sodic compounds impart to the outer lamp flame an intense <i>YELLOW</i> color. Small quantities of Na can by this means be detected in the presence of much K, the yellow flame overpowering the violet. ( <i>See par 51.</i> )

\* If CaH<sub>2</sub>O<sub>2</sub> is employed, it must be in the solid state, not in solution.

† This experiment is best performed by inserting a glass rod moistened

23. HOW TO ASCERTAIN THE PRESENCE OR ABSENCE OF EACH OF THE THREE MEMBERS OF THIS GROUP IN A SOLUTION WHICH CAN ONLY CONTAIN THESE THREE BASES.—The only test for a potassic compound which can be relied upon in the presence of an ammoniac one is the *flame reaction* (B 4), as the reagents which precipitate K from its solutions form precipitates similar in appearance with  $\text{NH}_4$ ; it is necessary, therefore, to get rid of the ammoniac compound, if one is present, before  $\text{H}_2\text{T}$  or  $\text{PtCl}_4$  can be employed as a *characteristic* test for K; consequently, ammonia has to be sought for first, and as the reagent employed for its detection would be an impediment (A 2) when searching for the other two members, we, on this account, test for ammonia in a *portion only* of the solution under examination; we divide, therefore, the solution into two parts, which we shall call A and B.

24. In A we examine for AMMONIA according to the method described in A 2 and par. 40, or by the one described in par. 42; these are characteristic tests for ammonia, distinguishing it from other substances. When ammonia is *absent* examine the B portion according to par. 25, and when it is *present* according to par. 26.

25. Examine for sodic and potassic compounds in the following way: A clean (see Precautions, par. 28) platinum wire is dipped into the solution, and then introduced into the flame of a Bunsen's gas lamp. If the flame is colored *yellow*, Na is present; if it is colored *violet*, it proves the absence of Na (C 4) and the presence of K (B 4). *If Na is present*, examine for K by the photo-chemical method (par. 46). The *presence of K* may be *confirmed* by adding to the solution under examination, which must be cold (B 3), a solution of  $\text{H}_2\text{T}$  or  $\text{NaHT}$  (see par. 44) in excess, and shaking the mixed liquid very violently, and then allowing it to rest for some time; if a crystalline precipitate appears after this, K is present (B 3). The time required for the appearance of the precipitate depends upon the amount of K in the solution; if the quantity of K is small, the precipitate may not appear until several hours after the addition of the reagent.

26. The solution must be evaporated to dryness and

with HCl into the mouth of the test-tube in which the decomposition of the ammoniac salt is being effected, and immediately withdrawing it. The HCl employed should not be concentrated, but should be diluted with an equal volume of water. (*Consult* par. 40.)

*ignited*, in order to volatilize the ammoniac substance (A 1); the ignition must be continued as long as any white fumes or smoke are evolved. If a residue remains after the expulsion of the ammoniac body, one or both of the other two members of the group are present; this residue must be dissolved in the smallest possible quantity of water, and examined for K and Na, in the way described in the preceding paragraph.

27. WHEN THE EXAMINATION IS NOT CONFINED TO THE ALKALIES, BUT ALL, OR, AT LEAST, SOME OF THE OTHER BASES HAVE TO BE SOUGHT FOR IN THE SOLUTION, the solution, after being freed from all the other bases but MgO and those of the first group, must be evaporated to dryness, and ignited, to expel the ammoniac salts, which have been added for their discovery. If a residue remain,\* after the vapor of the ammoniac salts has ceased to be evolved, it must be examined for K and Na, in the way described in par. 25. In this case—that is, when other bases besides those of the first group have to be sought for— $\text{NH}_4$  is to be tested for in a part of the *original solution*.

28. *The following precautions are to be attended to in the analysis of this group.*—Moist turmeric paper will turn brown by the mere exposure for a short time to the atmosphere of the laboratory, owing to the ammonia present in the air; this must be remembered in testing for ammonia in the manner described in par. 40. If the test-paper does not brown in the course of a few seconds or a minute, no ammoniac compound is present, and the browning which may occur by longer exposure must be regarded as due to the ammonia in the air. In testing for potassic or sodic compounds by the lamp-flame, it is necessary that the platinum wire should be perfectly clean; this is secured by keeping it in the lamp-flame until it imparts no color to it. Care should then be taken not to touch with the fingers that end of it on which the substance to be examined is to be placed. The flame reaction is not a reliable test for K in the presence of *organic matter*, as organic substances which burn with the separation of carbon color the flame violet; organic matter, if present, must be got rid of by *igniting* the substance if it is a solid, or if a solution by evaporating it to dryness, and then igniting the residue; in

\* A fixed residue is not a certain proof of the presence of potash or soda, as it may arise from the presence of one of the non-volatile acids, viz. phosphoric, boracic, or silicic acid.



either case the solid after ignition ought to be dissolved in a small quantity of water and filtered, if, after the water is added, any brownish-black particles appear. Young students seldom continue the ignition for the expulsion of the ammoniac salts sufficiently long, and, if these solids are not completely expelled, precipitates will be obtained with  $\text{H}_2\overline{\text{T}}$ ,  $\text{NaH}\overline{\text{T}}$ ,  $\text{PtCl}_4$ , which will be regarded as indicative of the presence of the potassic compound. The solution must be as concentrated as possible for the detection of K by  $\text{H}_2\overline{\text{T}}$ , or  $\text{NaH}\overline{\text{T}}$ , and the student is directed to par. 44 as regards the neutrality, acidity, and alkalinity of the liquids.

PROPERTIES OF THE METALS, THE OXIDES, THE SULPHIDES, THE CHLORIDES, THE NITRATES, THE SULPHATES, OF THIS GROUP.

29. *The metals.*—K, Na, and Li are lighter than  $\text{H}_2\text{O}$ . Li is the lightest of all known solids; the sp. gr. of Na is 0.985, that of K is 0.865, and that of Li 0.589. K melts at  $62.5^\circ \text{C}$ ., Na at  $95.5^\circ \text{C}$ ., and Li at  $180^\circ \text{C}$ . At a red heat, K and Na may be distilled; the vapor of K is a beautiful green color, that of Na is colorless; Li is volatile at high temperatures. These three metals oxidize on exposure to air; K is the most and Li the least oxidizable of the three; they decompose water at all temperatures, uniting with the oxygen and liberating the hydrogen; K decomposes it most rapidly, the hydrogen taking fire from the heat evolved by the combination of the metal with O. They combine directly with Cl, I, Br, S, etc.

30. *The oxides.*— $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{Li}_2\text{O}$  may be obtained either by introducing the metals into an atmosphere of oxygen, or by heating the metals and their hydric oxides together in equivalent proportions.  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$  melt at a red heat, and volatilize without decomposition at very high temperatures; these two oxides attract  $\text{H}_2\text{O}$  very rapidly from the air, and after they have become hydrated they cannot be dehydrated by heat alone. These anhydrous oxides are instantly converted into the hydrates on being brought into contact with  $\text{H}_2\text{O}$ , and it is in the form of hydrates they are employed in the laboratory and in the arts; the anhydrous oxides are, therefore, unimportant.

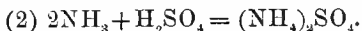
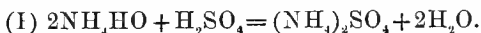
*The hydrates.*— $\text{KHO}$  and  $\text{NaHO}$  are usually prepared

from  $K_2CO_3$  and  $Na_2CO_3$ , by adding to boiling solutions of these salts  $CaH_2O_2$  until the clear solution no longer effervesces on the addition of  $HCl$  in excess. They may also be obtained, and it is in this way that  $LiHO$  is generally prepared, by adding to a solution of their sulphates a solution of  $BaH_2O_2$ . These hydrates are white solids; they melt below redness, and  $KHO$  and  $NaHO$  volatilize at a pale red heat;  $LiHO$  does not appear to volatilize at a white heat.  $KHO$  and  $NaHO$  absorb  $H_2O$  and  $CO_2$  from the air; by the absorption of the  $H_2O$  they are converted into syrupy liquids; as they become transformed into carbonates, the syrupy solution of the potash continues, whereas the soda becomes converted into an efflorescent paste, because  $K_2CO_3$  is deliquescent, and  $Na_2CO_3$  is not;  $LiHO$  absorbs  $CO_2$  from the air, but not  $H_2O$ . They are soluble in water and alcohol;  $LiHO$  is the least soluble of the three. Their aqueous solutions are very alkaline and absorb  $CO_2$  from the air. These alkalis are not reducible by  $H$ ;  $KHO$  and  $NaHO$  are reducible by  $C$ , the  $K$  and  $Na$  passing off in vapor; but  $Li$ , and the metals of the next group, although they have less affinity for  $O$  than  $K$  and  $Na$ , cannot be obtained in this manner, their oxides not being reducible by  $C$  because the metals are not sufficiently volatile to pass off in vapor. Heated in a current of  $Cl$ , they are converted into chlorides with disengagement of  $O$ . A current of  $Cl$  passed into their solutions converts them into a mixture of alkaline chlorides, and, according to the strength of the solution and the temperature, *alkaline hypochlorites* or *chlorates*; if the solutions are weak and not heated, hypochlorites are produced, when these conditions are reversed, the chlorates are formed. When fused with  $S$  at a temperature not above  $200^\circ C.$ , or if the  $S$  is boiled in their solutions, an alkaline hyposulphite and an alkaline polysulphide are formed; but if the reaction takes place at a red heat, an alkaline sulphate and an alkaline pentasulphide are produced. By the action of  $P$  on the alkalis, a mixture of alkaline hypophosphites and phosphides is formed. The alkalis dissolve alumina and silica, and attack glass and porcelain; the student will study the behavior of the insoluble basic oxides with the alkalis in the next groups.

31.  $NH_4$ .—This radical has never been obtained uncombined; when set free from its combinations it decomposes at the same moment, if it exists at all, into  $NH_3$  and  $H$ . Although it has never been isolated, the theory of its ex-

istence is considered to derive great support from the fact that Hg forms with  $\text{NH}_4$ , as it does with the true metals, an *amalgam*. This compound of Hg and  $\text{NH}_4$  is easily obtained by introducing sodium amalgam into a strong solution of  $\text{NH}_4\text{Cl}$ ; the Na rapidly dissolves by combining with the Cl, the liberated  $\text{NH}_4$  combining with the Hg; a soft, buttery mass is thus obtained, occupying an enormous volume compared with that of the Hg by itself.

32.  $\text{NH}_3$  and  $\text{NH}_4\text{HO}$ .—The name *ammonia* has been given to these two different compounds; the first is a gas, and the other is obtained by dissolving the gas in water; the same name was given to the gas and its solution, because it was considered the gas suffered no chemical change by its solution in water, inasmuch as it ( $\text{NH}_3$ ) is not only expelled from the solution by heat, but it even escapes from it at the ordinary temperature of the air; and the solution likewise retains the *smell* and other properties of the gas; hence the gas and its solution was regarded as the same *chemical* compound. They are now viewed as two distinct compounds. It is supposed that when  $\text{NH}_3$  is dissolved in  $\text{H}_2\text{O}$ , they enter into combination in equivalent proportions,  $\text{NH}_4\text{HO}$  (ammonic hydrate) being formed, corresponding to KHO and NaHO, the compound radical  $\text{NH}_4$  having functions similar to the simple bodies K and Na. The radical  $\text{NH}_4$  is supposed to exist in all ammonic salts, whether the salts be formed by the action of the acids on  $\text{NH}_4\text{HO}$ , or on  $\text{NH}_3$ ; thus—



$\text{NH}_3$  is remarkable for its pungent and peculiar smell, which is shared by the hydrate; the gas and the liquid have a strong alkaline reaction, and they both neutralize the strongest acids.

33. The *sulphides*, including the ammonic, may be obtained by dividing a solution of them into equal portions, and passing through one portion  $\text{H}_2\text{S}$  to saturation; an alkaline sulph-hydrate (MHS) is formed; on adding to this the other portion, the sulphide is produced; thus,  $\text{MHS} + \text{MHO} = \text{M}_2\text{S} + \text{H}_2\text{O}$ ;  $\text{K}_2\text{S}$  and  $\text{Na}_2\text{S}$  may be obtained by deoxidizing their sulphates with H or C at a red heat. Their solutions have an alkaline reaction, and are colorless at first, but after a time they become colored from absorbing O from the air, and becoming transformed

into a mixture of free alkali and a polysulphide. If heated in contact with the air or O, they become converted into sulphates. They readily dissolve S, and are converted into polysulphides. Acids decompose them with liberation of  $\text{H}_2\text{S}$ .

34. The *chlorides* may be formed by dissolving the alkalis or their carbonates in  $\text{HCl}$ ; these salts are soluble in water, and are sparingly soluble in spirit of wine; their solutions are neutral to test-paper.  $\text{NH}_4\text{Cl}$  does not volatilize at  $100^\circ \text{C}$ ., but at higher temperatures it volatilizes readily without decomposition; heated in open vessels,  $\text{KCl}$ ,  $\text{NaCl}$ , and  $\text{LiCl}$  volatilize at a red heat. The double salts they form with  $\text{PtCl}_4$  are noticed in pars. 41, 45, 55, 57.  $\text{KCl}$  and  $\text{NaCl}$ , when evaporated with excess of  $\text{H}_2\text{O}$  and  $\text{HNO}_3$ , are converted into oxalates and nitrates, and on igniting these two chlorides with  $(\text{NH}_4)_2\text{O}$ , alkaline carbonates are formed in considerable quantities.

35. The *nitrates* may be formed by adding  $\text{HNO}_3$  to the alkalis or their carbonates. They are readily soluble in  $\text{H}_2\text{O}$ , only slightly soluble in spirit of wine; their solutions are neutral to test-paper. They liquefy on application of heat; at a red heat  $\text{NaNO}_3$  and  $\text{KNO}_3$  are converted by the expulsion of one-third of their O into nitrites, and at a still stronger heat a further quantity of O, along with all the N, is expelled, and a mixture of the pro- and per-oxides of the metals remains; at  $108^\circ \text{C}$ .,  $\text{NH}_4\text{NO}_3$  liquefies, and at  $249^\circ \text{C}$ . it undergoes complete decomposition into  $\text{N}_2\text{O}$  and  $\text{H}_2\text{O}$ . The fixed alkaline nitrates heated with C and with S are converted into carbonates and sulphates, the N being expelled; when they are ignited with  $\text{NH}_4\text{Cl}$ , or in a current of dry  $\text{HCl}$  gas, they are converted into chlorides; and if *repeatedly* evaporated with excess of liquid  $\text{HCl}$ , they are completely converted into chlorides. If they are also repeatedly evaporated with  $\text{H}_2\text{O}$  in excess, they are converted into oxalates.

36. The *sulphates* may be formed by adding  $\text{H}_2\text{SO}_4$  to the alkalis or their carbonates, or by evaporating the nitrates or chlorides with  $\text{H}_2\text{SO}_4$ . They are soluble in water; the solution of those the general formula for which is  $\text{M}_2\text{SO}_4$  is neutral to test-paper; the solution of those whose general formula is  $\text{MHSO}_4$  is acid to test-paper.  $\text{K}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$ , at a white heat, are slightly decomposed;  $(\text{NH}_4)_2\text{SO}_4$  melts at  $140^\circ \text{C}$ ., and between  $260^\circ \text{C}$ . and  $315^\circ \text{C}$ . it volatilizes and undergoes decomposition,  $(\text{NH}_4)_2\text{SO}_3$  being among the

products. Fe decomposes  $K_2SO_4$  and  $Na_2SO_4$  at a red heat, the alkalies are liberated, and a mixture of sulphide and oxide of iron formed; they are converted into chlorides by ignition with  $NH_4Cl$ , and we have already noticed (33) they are deoxidized by ignition with C. One of the two atoms of radical in these sulphates can be replaced by one of the other radicals, or by H; thus,  $NH_4NaSO_4$ ,  $KHSO_4$ , etc.

37. *General characters of the salts of this group.*—The metals of this group, compared with those of the other groups, furnish the largest number of salts soluble in water; the sodic salts are almost all soluble in  $H_2O$ , hence there are no very good direct tests for sodic compounds, and owing to the greater number of the salts of these metals being soluble, we have no group or general reagents for this group as we have for the other groups. Not only are the oxides soluble in  $H_2O$ , but also their sulphides, sulphates, oxalates, carbonates, phosphates, nitrates, and other salts. The sparing solubility of lithic phosphate and carbonate in  $H_2O$  distinguishes it from the other members of the group, and renders it more nearly allied in this respect to the next group. The solutions of the sulphides and carbonates, as well as the solution of the alkalies themselves, restore the blue color to reddened litmus, and impart an intensely brown tint to turmeric paper. The salts of these bases are colorless, provided the constituent acid be so.

#### REMARKS ON THE INDIVIDUAL MEMBERS OF THE GROUP, WITH ADDITIONAL SPECIAL TESTS.

38.  $NH_4$  and its compounds.— $NH_3$ , we have already stated, is remarkable for its pungent smell, and it exerts a powerfully corrosive action on moist animal tissues, hence serious consequences might arise from inhaling a considerable quantity. The white fumes produced when  $NH_3$  is brought into contact with a volatile acid are due to the formation of a solid ammoniac salt. All ammoniac salts containing volatile acids, on being heated, volatilize either with or without decomposition; but the ammoniac salts of the non-volatile acids, viz., phosphoric, boracic, and silicic, are decomposed by heat; the ammonia escapes, but the non-volatile acid remains behind.

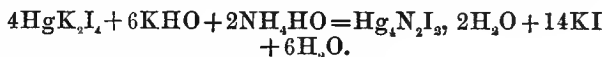
39. When organic substances containing N decay and putrefy, ammoniac carbonate is constantly produced; the

same salt is likewise formed when nitrogenized organic substances are submitted to destructive distillation.

40. The following modification of the test (A 2) for ammonia is to be preferred: If the *substance* is in solution, mix it in a small beaker, with sufficient  $\text{CaH}_2\text{O}_2$  to render the mixture solid; but if it is a *solid*, moisten it slightly with  $\text{H}_2\text{O}$  before mixing it in the beaker with excess of  $\text{CaH}_2\text{O}_2$ . The beaker is covered, after the mixing, with a glass plate, on the lower side of which adheres a small piece of moist turmeric or moist reddened litmus paper.

41.  $\text{PtCl}_4$  produces in neutral and acid ammoniac, as in potassic solutions, a yellow crystalline precipitate  $2\text{NH}_4\text{Cl}$ ,  $\text{PtCl}_4$ , very sparingly soluble in alcohol.

42. If a solution of  $\text{HgK}_2\text{I}_4$  in  $\text{KHO}$  be added in excess to a liquid containing a trace of  $\text{NH}_4\text{HO}$  or its salts, it assumes a brownish tinge or furnishes a brown precipitate, according as the proportion of the ammoniac compound is less or more, tetramercuric diammoniac diniodide being formed, thus:—



This test is called Nessler's test.

*Characteristic.*—The reactions with  $\text{CaH}_2\text{O}_2$  (40), and with Nessler's test.

43. *K and its compounds.*—K is of a bluish-white color; it is brittle at  $0^\circ\text{C}$ .; a little above this temperature it is malleable; at  $16^\circ$  it is soft; at  $62.5^\circ$  it is liquid, and at a red heat it may be distilled; when freshly cut, it possesses considerable lustre, but instantly oxidizes on exposure to the air; it can only be preserved in the metallic state by keeping it in some liquid, like coal naphtha, which contains no oxygen, or in exhausted hermetically sealed glass tubes. It occurs in felspar, mica, etc., as silicate, in combination with aluminic and other silicates. It is also found as sulphate, nitrate (saltpetre), and in a mineral called carnallite, which is a double hydrated potassic and magnesian chloride ( $\text{KCl}$ ,  $\text{MgCl}_2$ ,  $6\text{H}_2\text{O}$ ), which occurs above the bed of rock salt at Stassfurth, near Magdeburg.

44.  $\text{NaHT}^*$  is a much more delicate test for K than  $\text{H}_2\text{T}$ , because  $\text{KHT}$  in neutral solutions is soluble in acids,

\* My friend, Mr. W. Plunkett, suggested the employment of  $\text{NaHT}$ . See "Chemical Gazette," vol. xvi. p. 217.

and an acid must be set free whenever  $H_2T$  is added to a solution containing a potassic salt. If the solution is acid, the free acid must be expelled, if practicable, by evaporation or ignition; or if not expelled, it must be neutralized with  $NaHO$  or  $Na_2CO_3$  before testing for  $K$  either with  $NaHT$  or  $H_2T$ .  $NaHT$  cannot, of course, replace  $H_2T$  as a test for  $K$  when the solution to be tested contains a free alkali, because  $KHT$  is soluble in free alkalis; but when the bases of the other groups are sought for, the solution cannot be alkaline when we arrive at the examination for  $K$ , and it is not often that we have to deal with an alkaline solution, even when the alkalies are the only bases that have to be examined for.

45.  $PtCl_4$  produces, in neutral and acid solutions of  $K$ , a yellow crystalline precipitate\* of  $2KCl, PtCl_4$ . The presence of  $HCl$  promotes the formation of this precipitate. It is slightly soluble in water, but wholly insoluble in alcohol. This is a very delicate test for any potassic compound; the best method of applying it is to mix the solution with  $PtCl_4$ , evaporate to dryness upon a water-bath, and treat the residue with alcohol; the excess of  $PtCl_4$  dissolves in the alcohol, coloring the solution yellow;  $2KCl, PtCl_4$  is left undissolved as a yellow crystalline precipitate. The addition of  $PtCl_4$  should always be preceded by that of  $HCl$ , to convert the potassic compound into the chloride, if it should not exist already in that form.

46. If a small particle of a potassic compound be introduced on the loop of a platinum wire into the flame of a *Bunsen's gas-lamp*, it will, if volatile at the temperature of the flame, color the part of the flame above the sample *blue-violet*; if the substance examined contains a sodic as well as a potassic compound, the yellow color imparted to the flame by the sodic compound overpowers and obscures the violet tint produced by the potassic one. But  $K$  can be detected in the presence of  $Na$  (or  $Li$ ) if we look at the flame through deep blue cobalt glass;† through this colored

\*  $PtCl_4$  gives with iodine a dark red color; and as this color prevents the yellow precipitate of  $2KCl, PtCl_4$  from being distinctly seen, iodine should be expelled, if present, before testing for  $K$  by this reagent. To expel it, evaporate to dryness with *concentrated*  $HNO_3$ ; dissolve the residue in water, and add  $HCl$  and  $PtCl_4$ , and then proceed in the usual way.

† The cobalt blue glass can be obtained at the operative chemists. Before using the glass, it must first, of course, be ascertained how small a quantity of potash mixed with soda (or lithia) it will clearly indicate.

glass no colored rays from Na (or Li) can pass, but it transmits those peculiar to K. The flame, when viewed through this colored glass, is of an intense violet color, and is even visible when one part of potash is present with two hundred parts of soda. As all substances which make flame luminous, especially all organic substances which burn with separation of carbon, give the same violet color, these substances must first be removed by heat before the color of the flame can be used as a test for K.

47. The potassic flame may be viewed through the indigo prism instead of the blue glass; the flame appears through the prism of *sky blue*, then *violet*, and at last of an intense *crimson red*, even when seen through the thickest layers of solution; admixtures of Na or Ca do not hinder the reaction.

48. The potassic flame viewed through the violet-colored glass appears violet, and through the green colored glass blue-green.

49. The more volatile the salt, the more intense is the coloration it imparts to the flame; potassic chloride and potassic nitrate volatilize rapidly, the carbonate and sulphate less rapidly, and the phosphate still more slowly, but they all of them distinctly show the reaction, though decreasing in degree. The sensibility of the test may, in many cases, be increased by moistening the substance under examination with  $\text{H}_2\text{SO}_4$ , drying the substance at the border of the flame, and then introducing it into the melting space. With silicates and other difficultly volatile potassic compounds the reaction is best secured by fluxing it with pure gypsum in the melting space; there is formed a calcic silicate and volatile potassic sulphate which color the flame. It is advisable to ignite decrepitating salts in a platinum spoon before attaching them to the loop of the platinum wire.

*Characteristic.*—The flame test, the reaction with  $\text{PtCl}_4$  and  $\text{NaHTl}$ .

50. *Na and its compounds.*—The color of this metal is bluish-white; in properties it much resembles K. The salts of this base, with a few exceptions, are very soluble; the means we have of detecting it are therefore limited. It exists in the mineral kingdom as CHLORIDE (*kitchen salt*), SULPHATE (*Glauber's salt*), BORATE (*borax or tincal*), NITRATE and CARBONATE. It likewise forms a constituent of many SILICEOUS MINERALS.



51. If a small particle of a sodic compound be introduced, on the loop of a platinum wire, into the melting space of the flame of a *Bunsen's gas-lamp*, it will, if volatile at the temperature of the flame, color the part of the flame above the sample intense yellow; this is the most characteristic test for sodic compounds. If the sodic flame is made to illuminate a crystal of potassic bichromate, this salt appears perfectly colorless and transparent, and with an adamantine lustre. The following reaction is even more delicate. A piece of paper about a centimètre square is coated with red mercuric iodide, and placed upon a small holder, which is movable on an arm, also movable, attached to the chimney of the lamp. When the least quantity of  $\text{NaHO}$ ,  $\text{Na}_2\text{SO}_4$ , or  $\text{NaCl}$ , is introduced into the melting space of the flame, the red iodide becomes white, with a faint tinge of fawn color. The glaring contrast of these colors is apparent when the paper is lit up by being placed close to the red-hot wire and bead, and the wire then placed in the flame, so that the bead only reaches the melting space. Potassic, lithic, and calcic compounds do not interfere with this reaction.

52. The sodic flame appears *orange-yellow*, through the green glass, even with the smallest quantities. This glass is particularly adapted to the recognition of all sodic compounds (Merz).

53. Although the sodic salts are a little less volatile than the potassic salts, they display, with regard to their relative volatility, and the influence of  $\text{H}_2\text{SO}_4$  and pure gypsum in increasing their sensibility, the same behavior as the potassic ones.

54. Di-hydric di-potassic metantimoniate ( $\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7$ ) produces, in neutral or alkaline solutions of sodic salts, a white crystalline precipitate of  $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$ . In concentrated solutions the precipitate is formed immediately; but from dilute solutions it separates only after the lapse of some time. Violent agitation of the fluid promotes the separation of the precipitate. Acid solutions decompose the potassic salt, antimonious acid being precipitated; free acids must therefore be first neutralized with potash before this test can be applied.  $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$  is soluble in  $\text{K}_2\text{CO}_3$ ; if this substance be present in the solution it must be nearly saturated with acetic acid.

55. The double chloride of  $2\text{NaCl}$ ,  $\text{PtCl}_4$  is soluble in alcohol, and very soluble in water; therefore  $\text{PtCl}_4$  produces

no insoluble salt with sodic compounds, either in an aqueous or alcoholic solution.

*Characteristic.*—The flame reaction.

56. *Li and its compounds.*—Lithia occurs in certain minerals, particularly in spodumene, petalite, and lepidolite.

57.  $\text{Na}_2\text{HPO}_4$  produces in not over dilute solutions of lithic salts, upon boiling, a heavy white crystalline precipitate of  $\text{Li}_3\text{PO}_4$ ; if the solution is then evaporated to dryness, and the residue treated with cold water, the lithic phosphate remains undissolved. We can, therefore, in this way distinguish Li from, and in the presence of, K and Na.  $\text{LiCl}$  forms with  $\text{PtCl}_4$  a double salt,  $2\text{LiCl} \cdot \text{PtCl}_4$ , which is even more soluble in water than the corresponding sodic salt,  $2\text{NaCl} \cdot \text{PtCl}_4$ .

58. "If a lithic salt, particularly  $\text{LiCl}$ , is exposed on a platinum wire in the melting space of the flame of a Bunsen's gas-lamp, the outer flame shows a strong CARMINE tint. Presence of sodic salts, but not potassic salts, conceals this reaction."

59. If the lithic flame be viewed through the indigo prism, it appears through the thinnest layer of the indigo solution of a *carmine-red*, which, with increasing thickness of the solution, becomes *gradually feebler*, and *disappears* before the thickest layers pass before the eye; whereas the potassic flame appears through the thinnest layer of the indigo solution of a *sky-blue*, then *violet*, and at last of an intense *crimson-red*, even when seen through the thickest layers of the solution. Admixtures of sodic or calcic compounds do not hinder the reaction of either the Li or K.

60. As of all lithic compounds the carbonate and chloride give the most intensely colored flame, it is only necessary to mark on the prism the place at which the lithic rays from these salts disappear, to obtain a space above this mark which transmits only red potassic rays. As this part of the prism acts in the same way as a thick cobalt glass in detecting potassic compounds in the presence of sodic ones, the cobalt glass can be dispensed with for detecting K.

61. Lithia with an admixture of potash is detected by bringing a sample into the melting space, and comparing its flame with that of a sample of pure potash placed side by side with it in the melting space. With thin layers of the solution the lithic flame appears redder than the pure potassic flame; with somewhat thicker layers the flames are equally red, if the proportion of lithia to potash be very small; if the lithia be in excess, the intensity of the red lithic flame sensibly diminishes with thicker layers, while the red flame of potash is scarcely weakened. In this manner a few thousandths of lithia may be detected in the presence of potash. Soda has almost no influence on the reaction.

62. *Characteristic.*—The flame test and the reaction with  $\text{Na}_2\text{HPO}_4$ .

63. Answers to the following exercises must be written out.

#### EXERCISES.

1. In what are K and Na found in nature?

2. Describe the different parts of a flame, and explain the action of those in blow-pipe experiments.

3. Describe a method for the preparation of sodic hydric tartrate.

4. Knowing that  $N_2O$  is produced by subjecting dry  $NH_4NO_3$  to heat, what gas would you infer would be produced by subjecting  $NH_4NO_2$  to heat?

5. Under what circumstances would you employ tartaric acid in preference to sodic hydric tartrate as a test for K?

6. Describe some of the physical and chemical properties of K and Na.

7. Account for the formation of ammoniac sulphide and carbonate in the manufacture of gas from coal.

8. State how you would prepare  $PtCl_4$ .

9. Describe the preparation and application of the test called "Nessler's test."

10. Do solid KHO and NaHO undergo any change on exposure to air; and if so, name the changes and any differences which they may exhibit.

11. What are the characteristic tests for K, Na, and  $NH_4$ ?

12. How are the alkaline hydrates prepared?

13. Describe as many methods as you are able for distinguishing K from Na.

14. Describe a method for the preparation of  $K_2H_2Sb_2O_7$ .

15. Show by means of an equation the chemical changes which take place in the preparation of  $KClO_3$  from the action of Cl on KHO.

16. Show by means of equations the action of sulphur on the fixed alkalis at different temperatures, and the action of phosphorus on the fixed alkalis.

17. To what are the terms "precipitation," and "evaporation," and "distillation" applied?

18. What is the difference between a simple and a chemical solution?

## SECOND GROUP.

BARIC OXIDE ( $BaO$ ), STRONTIC OXIDE ( $SrO$ ), CALCIC OXIDE ( $CaO$ ), MAGNESIC OXIDE ( $MgO$ ).

*Solutions for the reactions.*— $BaCl_2$ ,  $SrCl_2$ ,  $CaCl_2$ ,  $MgSO_4$ , in water.

64. "Baryta," "Strontia," "Lime," "Magnesia," are names very frequently given to these oxides, they are also employed occasionally to signify the hydrates of the oxides; but if the term *caustic* be employed along with them,

they refer then exclusively to the anhydrous oxides. These oxides and their hydrates are called "the alkaline earths," and their salts are called "the salts of the alkaline earths."

65.  $(\text{NH}_4)_2\text{CO}_3$  precipitates Ba, Sr, and Ca completely from their solutions as carbonates, but it precipitates Mg *only partially*, and this partial precipitation is prevented, at least for a time, if  $\text{NH}_4\text{Cl}$  is present in the solution (see par. 108). Owing to this difference in their behavior with  $(\text{NH}_4)_2\text{CO}_3$ , the group is subdivided; the members of the first division are BaO, SrO, and CaO; MgO forms the second. The *group reagent* for the first division is  $(\text{NH}_4)_2\text{CO}_3$ , its addition is *preceded* by that of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{HO}$ . The *reagent* for MgO is  $\text{Na}_2\text{HPO}_4$ , but as it also precipitates the members of the first division, it can only be employed for MgO after the removal, or in the absence, of BaO, SrO, and CaO.

66. *Examination for the members of the first division.*—When a solution is examined for the members of this division *only*, the group reagent must be added, and as directed at par. 369.

67. The precipitate produced by the group reagent, after being well washed, must be dissolved in *acetic acid*, and the solution divided into two parts, which we shall call A and B.

68. *Add a solution of (not too little)  $\text{CaSO}_4$  to the A portion.*—As  $\text{CaSO}_4$  precipitates Ba *immediately*, Sr *after the lapse of some time*, and Ca *not at all* (see D 1, E 1, and F 1), one of three cases will occur on the addition of  $\text{CaSO}_4$  to the A portion; either there will be *no precipitate*, or there will be *one after the lapse of some time*, or there will be an *immediate one*. If there is no precipitate, examine according to par. 69; if there is one after the lapse of some time, examine according to par. 70; if there is one immediately, examine according to par. 71.

69. As Ba and Sr are absent, add to the B portion  $\text{NH}_4\text{HO}$  and a solution of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ ; if a precipitate is produced, Ca is present.

TABLE II.

BEHAVIOR OF THE MEMBERS OF THE FIRST DIVISION OF THE  
SECOND GROUP WITH THE SPECIAL REAGENTS.

BaO.	SrO.	CaO.
D 1. $\text{CaSO}_4$ , in solution, precipitates Ba <i>immediately</i> , from its solutions, as $\text{BaSO}_4$ , which is insoluble in acids and alkalis.	E 1. $\text{CaSO}_4$ , in solution, precipitates Sr <i>after the lapse of some time</i> ,* from its solutions, as $\text{SrSO}_4$ , which is almost absolutely insoluble in acids and alkalis.	F 1. $\text{CaSO}_4$ produces <i>no</i> precipitate in solutions of Ca.
D 2. $\text{K}_2\text{CrO}_4$ , in solution, produces, in neutral and alkaline solutions of Ba, a pale yellow precipitate of $\text{BaCrO}_4$ , insoluble in the alkalis and acetic acid, soluble in $\text{HCl}$ and $\text{HNO}_3$ .	E 2. $\text{K}_2\text{CrO}_4$ , in solution, produces in <i>concentrated</i> , but not in <i>dilute</i> , solutions of Sr, or such as contain <i>free acetic acid</i> , a bright yellow precipitate of $\text{SrCrO}_4$ .	F 2. $\text{K}_2\text{CrO}_4$ , in solution, produces no precipitate in solutions of Ca, $\text{CaCrO}_4$ being soluble.
D 3. $\text{H}_2\text{SO}_4$ and the <i>soluble sulphates</i> behave in the same manner in solutions of Ba as $\text{CaSO}_4$ .	E 3. $\text{H}_2\text{SO}_4$ and the <i>soluble sulphates</i> precipitate Sr from its solutions, as $\text{SrSO}_4$ . The precipitate will not appear immediately, unless the solution be very concentrated.	F 3. $\text{H}_2\text{SO}_4$ and the <i>alkaline sulphates</i> cause only in concentrated solutions of Ca a partial precipitate of $\text{CaSO}_4$ , which redissolves completely in a large amount of water.
D 4. $\text{H}_2\text{C}_2\text{O}_4$ , in solution, produces only in concentrated solutions of Ba a white precipitate of $\text{BaC}_2\text{O}_4$ , soluble in acids. The addition of $\text{NH}_4\text{HO}$ renders this reaction therefore more susceptible.	E 4. $\text{H}_2\text{C}_2\text{O}_4$ , in solution, precipitates, even from dilute solutions of Sr, a white precipitate of $\text{SrC}_2\text{O}_4$ . The addition of $\text{NH}_4\text{HO}$ promotes the formation of the precipitate.	F 4. $\text{H}_2\text{C}_2\text{O}_4$ , in solution, throws down from neutral solutions of Ca, even if highly diluted, a precipitate of $\text{CaC}_2\text{O}_4$ . The addition of $\text{NH}_4\text{HO}$ renders this reaction more delicate.

70. Ba is *absent*; Sr is, and Ca may be, *present*. The presence or absence of Ca cannot be determined, as long as any Sr remains in solution; because the reagents, which precipitate Ca, precipitate Sr also (E 3, F 3, E 4, F 4).

\* The formation of the precipitate is much promoted by agitation.

We add, therefore, to the B portion *dilute*  $\text{H}_2\text{SO}_4$ , which precipitates all the Sr (E 3), and only a small portion of Ca in a concentrated and none at all from a dilute solution (F 3); in any case, sufficient Ca remains in solution for detection. Filter off from the precipitate produced by the  $\text{H}_2\text{SO}_4$ , after sufficient time (one or two hours) has been allowed for the precipitation of the  $\text{SrSO}_4$ , and add to the filtrate  $\text{NH}_4\text{HO}$  in excess, and then  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ , which will cause a precipitate if Ca is present.

71. Ba is, and Sr and Ca may be, present. As  $\text{CaSO}_4$  cannot be employed to detect Sr in the presence of Ba, and as Ba causes a precipitate with all the reagents which precipitate Sr and Ca, the former must be got rid of before we can ascertain the absence or presence of the two latter substances. For this purpose,  $\text{K}_2\text{CrO}_4$  must be added to the B portion, which precipitates Ba only (D 2, E 2, F 2); filter, and to the filtrate\* (which will be of a yellow color; from the excess of  $\text{K}_2\text{CrO}_4$ , if the Ba has been completely precipitated) add  $\text{NH}_4\text{HO}$  in excess and  $(\text{NH}_4)_2\text{CO}_3$ , and warm the solution; if a precipitate is produced, it may be due to the presence both of Sr and Ca; if no precipitate is produced, Sr and Ca are absent. If a precipitate is produced, wash it until all excess of  $\text{K}_2\text{CrO}_4$  has been removed, then dissolve it in acetic acid, filter, if necessary, through a very small filter, and add to the clear solution not too small a quantity of the dilute solution of  $\text{K}_2\text{SO}_4$ ,† after which addition the solution must be well agitated; if the  $\text{K}_2\text{SO}_4$  produces a precipitate, after the lapse of some time, Sr is present. If the  $\text{K}_2\text{SO}_4$  solution has produced a precipitate, add some dilute  $\text{H}_2\text{SO}_4$  to complete the precipitation, and allow sufficient time (one or two hours) for the complete separation of the  $\text{SrSO}_4$  before filtering; add to the filtrate, or to the solution, without filtering, if  $\text{K}_2\text{SO}_4$  has produced no precipitate,  $\text{NH}_4\text{HO}$  in excess and  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ ; if this last reagent produces a precipitate, Ca is present.‡

\* It is absolutely necessary to have the filtrate from the  $\text{BaCrO}_4$  perfectly bright and transparent, which sometimes is troublesome to obtain. See filtration in Part III.

† Care must be taken to make the solution of  $\text{K}_2\text{SO}_4$  of the strength directed in the list of reagents. Of that strength, it contains the same quantity of  $\text{SO}_4$  as a saturated solution of  $\text{CaSO}_4$  contains in a like quantity of liquid; it is, therefore, sufficiently strong to precipitate SrO, but not to precipitate CaO.

‡ For another method for the separation and detection of these three substances, and for the photo-chemical method, the student is referred to pars. 99 and 101.

72. The filtrate from the  $(\text{NH}_4)_2\text{CO}_3$  or the solution with which  $(\text{NH}_4)_2\text{CO}_3$  has failed to give a precipitate, must be examined for Mg as directed at par. 372.

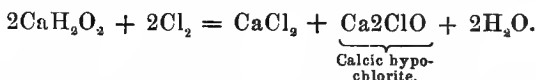
73. *The following precautions are to be attended to in the analysis of this group:* The solution of  $\text{CaSO}_4$  must be added in not too small a quantity, and it must always be added in the cold, as this reagent is less soluble in hot than cold water. Time must be allowed for the formation of the precipitate produced by this reagent in solutions of Sr, the formation of which is much promoted by agitation. In separating Sr from a solution by  $\text{K}_2\text{SO}_4$ , the liquid ought not to be filtered immediately, but a due time allowed for the complete separation of the precipitate from the solution; and the solution ought not to be warmed, owing to the less solubility of  $\text{CaSO}_4$  in hot than cold water.

PROPERTIES OF THE METALS, THE OXIDES, THE SULPHIDES, THE CHLORIDES, THE NITRATES, THE SULPHATES, OF THIS GROUP.

74. The *metals* are heavier than water, and decompose it, at common temperatures, although Mg does so only slowly, with the formation of the oxides and evolution of H. Mg is nearly as volatile as Zn; the other three are not sensibly volatile. Ba, Sr, and Ca, oxidize on exposure to dry as well as moist air, but Mg oxidizes only in moist air. They dissolve easily in dilute  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$ , with disengagement of H; concentrated  $\text{HNO}_3$  is almost without action on Sr, even when boiled upon it. They combine with Cl, I, Br, O, S, P, etc., at ordinary or more elevated temperatures. Mg unites directly with N; and when ignited in air or O it takes fire, burning with a dazzling light, which is remarkably rich in chemical rays; it is on this account employed for photographic purposes.

75. The *oxides* may be formed either by the ignition of their carbonates, nitrates, or any of their salts containing volatile acids, or by expelling the  $\text{H}_2\text{O}$  from their hydrates by heat. BaO, SrO, and MgO, *fuse* only at the very highest temperatures, as in the oxyhydrogen blowpipe flame, but even in this intense heat CaO exhibits no signs of fusing. These oxides are not reduced by H or by C. BaO, SrO, and CaO, when heated with S, are converted into a mixture of sulphate and sulphide, but MgO is not altered by it.

Dry Cl converts them, with the exception of  $\text{MgO}$ ,\* at a full red heat into chlorides, with disengagement of O.  $\text{BaO}$ ,  $\text{SrO}$ , and  $\text{CaO}$ , combine readily with  $\text{H}_2\text{O}$ , forming hydrates; the combination is attended with disengagement of heat.  $\text{MgO}$  combines only slowly with  $\text{H}_2\text{O}$ , and no sensible disengagement of heat attends the combination. These hydrates can also be prepared by dissolving one of their soluble salts in a boiling solution of  $\text{NaHO}$ ;  $\text{BaH}_2\text{O}_2$  is very frequently prepared by heating a solution of  $\text{BaS}$  with  $\text{CuO}$ .  $\text{BaH}_2\text{O}_2$  is soluble in twenty times its weight of cold, and three times its weight of boiling, water;  $\text{SrH}_2\text{O}_2$  is soluble in fifty times its weight of cold, and 2.4 times its weight of boiling, water;  $\text{CaH}_2\text{O}_2$  dissolves in about 700 pts. of cold, and is less soluble in boiling, water;  $\text{MgH}_2\text{O}_2$  is almost insoluble in water; the aqueous solutions of these hydrates have an alkaline reaction. In their dry state and in solution they attract  $\text{CO}_2$  from the air, and become converted into carbonates. When Cl is passed over them in their dry state, or into solutions of them, without the aid of heat, bleaching compounds (hypochlorites) are formed, thus:—



They, like the alkalis, are converted by the Cl at higher temperatures into chlorates and chlorides. By the action of S upon the hydrates, a sulphide and a hyposulphite are formed, thus:—



76. The metals of this group furnish no other *basic* oxides but these.

77. The *sulphides* may be prepared by mixing their sulphates with C or carbonaceous matter, as starch, and subjecting the mixture to a strong heat, or by passing the vapor of  $\text{CS}_2$  over the oxides in a state of ignition;  $\text{MgS}$ , on account of its sparing solubility, may be prepared by adding a solution of  $\text{K}_2\text{S}$  to a solution of its sulphate. They are soluble,  $\text{MgS}$  only sparingly, in water, and are

\*  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ , and the other oxides termed earths, are not acted on by Cl; but if they are mixed with C they are then converted in an atmosphere of dry Cl into chlorides; the affinity of the C for the O, and the affinity of Cl for the metal effecting the transformation of these metallic oxides into chlorides.



decomposed by it into sulph-hydrates and hydrates of the oxides; the solutions possess an alkaline reaction. Exposed to the air, they absorb  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , and are converted into carbonates with evolution of  $\text{H}_2\text{S}$ ; they are also decomposed with evolution of  $\text{H}_2\text{S}$  by  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{CO}_2$ , etc. Heated in a current of air they are converted into sulphates; in a current of  $\text{Cl}$  the chloride of the metal and chloride of sulphur are formed, in the moist state the chloride of the metal is also formed, but  $\text{S}$  is set free. If  $\text{H}_2\text{S}$  is passed into their solutions, they combine, forming hydric sulphides ( $\text{M}''\text{S}, \text{H}_2\text{S}$ ) which are soluble; these hydric sulphides are also obtained by passing  $\text{H}_2\text{S}$  into solutions of the oxides.  $\text{CaS}$ ,  $\text{H}_2\text{S}$ , and  $\text{MgS}$ ,  $\text{H}_2\text{S}$ , are decomposed by boiling  $\text{H}_2\text{O}$  into their hydric oxides and  $\text{H}_2\text{S}$ . A greater number of the sulphides than of the oxides of these metals have been formed.

78. The *chlorides* may be prepared by dissolving the oxides, their hydrates, the carbonates, or the sulphides, in dilute  $\text{HCl}$ ;  $\text{BaCl}_2$  may be obtained by fusing together 1 part of  $\text{CaCl}$  and 2 pts. of powdered native  $\text{BaSO}_4$ ;  $\text{CaSO}_4$  and  $\text{BaCl}_2$  are formed, and may be separated by treating the fused mass rapidly with boiling water. They are soluble in  $\text{H}_2\text{O}$ ;  $\text{BaCl}_2$  does not deliquesce in moist air, and is insoluble in absolute alcohol; the other three deliquesce in moist air, and are soluble in absolute alcohol; their aqueous solutions are neutral to test-paper;  $\text{CaCl}_2$ , from its extreme deliquescence, is frequently employed for desiccating substances. They all melt when heated;  $\text{CaCl}_2$  and  $\text{MgCl}_2$  melt at a low red heat.  $\text{MgCl}_2$  is *partially* decomposed during the evaporation of its solution,  $\text{HCl}$  and  $\text{MgO}$  being formed; by adding  $\text{NH}_4\text{Cl}$  to the solution before commencing the evaporation, this decomposition is prevented, as a double chloride ( $\text{MgCl}_2, \text{NH}_4\text{Cl}$ ) is formed, which does not lose acid on evaporation;  $\text{MgCl}_2$  forms, as we see in this case, double chlorides with the alkaline chlorides. The chlorides of this group are not decomposed on being heated in a current of  $\text{H}$ .

79. The *nitrates* may be formed by dissolving the oxides, their hydrates, or the carbonates, in dilute  $\text{HNO}_3$ . They are soluble in water;  $\text{Ca}(\text{NO}_3)_2$  and  $\text{Mg}(\text{NO}_3)_2$  deliquesce in moist air, and are soluble in alcohol; the other two do not deliquesce, and are insoluble in alcohol. These nitrates are decomposed, as we have seen, by heat (75).

80. The *sulphates*.— $\text{BaSO}_4$  is insoluble in  $\text{H}_2\text{O}$  and in acids, but it is rendered notably soluble in  $\text{H}_2\text{O}$  by the

presence of several salts, especially  $\text{MgCl}_2$  and  $\text{NH}_4\text{NO}_3$ .  $\text{SrSO}_4$  is sparingly soluble in  $\text{H}_2\text{O}$ , 1 pt. dissolving in 6895 pts. of  $\text{H}_2\text{O}$ ; its solubility is *increased* by the presence of  $\text{NaCl}$ , and *decreased* by the presence of alkaline sulphates; or, if the water is acidulated with  $\text{H}_2\text{SO}_4$ , it is rather more soluble in dilute  $\text{HCl}$  and in dilute  $\text{HNO}_3$  than in pure water.  $\text{Ba}$  and  $\text{Sr}$  are not completely precipitated from solutions containing metaphosphoric acid by  $\text{H}_2\text{SO}_4$ , and alkaline citrates impede their precipitation by  $\text{H}_2\text{SO}_4$  in a high degree, but the precipitation appears on the addition of  $\text{HCl}$ .  $\text{CaSO}_4$  is soluble in from 250 to 300 pts. of cold water; its *solubility* is increased if the water is acidulated with  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ , or  $\text{HNO}_3$ ; its solubility is also increased in the presence of  $\text{NH}_4\text{Cl}$ ,  $\text{NaCl}$ , and other substances; it is less soluble in hot than cold water.  $\text{MgSO}_4$  is readily soluble in water, is insoluble in absolute alcohol, and only slightly soluble in dilute spirit. The aqueous solutions of these salts do not alter vegetable colors. These sulphates, we have noticed, if mixed with  $\text{C}$  and strongly heated, are deoxidized. Heated to intense redness,  $\text{MgSO}_4$  loses part of its acid, the other three are not altered at that heat. Solutions of the alkaline carbonates in the *cold* decompose  $\text{SrSO}_4$ ,  $\text{CaSO}_4$ , and  $\text{MgSO}_4$ , but they have only a slight decomposing action in the cold on  $\text{BaSO}_4$ ; but when boiling, and upon repeated application, they decompose completely this baric salt. These sulphates are also readily decomposed on being fused with alkaline carbonates.

81. *General characters of the salts of this group.*—The salts of these metals are colorless unless the acid is colored. The soluble neutral salts are neutral or alkaline, not acid, to test-paper. The soluble baric, strontic, and calcic salts, with the exception of the chlorides, are decomposed upon ignition; all the soluble magnesian salts are decomposed, the sulphate partially, upon ignition, some of them even on the simple evaporation of their solutions. Most of the insoluble salts of this group are dissolved by dilute  $\text{HCl}$ .  $\text{MgO}$  differs from the other members, not only by its non-precipitation by  $(\text{NH}_4)_2\text{CO}_3$  and by  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  in the presence of ammoniac salts, but by the difficult solubility of its hydrate, and the ready solubility of its sulphate. A larger number of the salts of this group are insoluble than those of the first; the insolubility of the carbonates, phosphates, and oxalates, especially distinguish this group from the first; they are distinguished from the following groups by

the solubility of their sulphides; they are therefore neither precipitated by  $(\text{NH}_4)_2\text{S}$  nor by  $\text{H}_2\text{S}$ .

REMARKS ON THE INDIVIDUAL MEMBERS OF THE GROUP, WITH  
ADDITIONAL SPECIAL TESTS.

82. *Barium and its compounds*.—Ba, according to Davy, is a silver-white metal, with less lustre than cast-iron. According to Matthiesen, it is a powder of a yellow color. BaO is a grayish-white friable mass.  $\text{BaH}_2\text{O}_3$  is a white powder; it crystallizes from its solutions in colorless crystals, containing 8 at. of water of crystallization.

83. The principal minerals of Ba are the SULPHATE (*heavy spar*), and the CARBONATE (*witherite*).

84.  $\text{H}_2\text{SiF}_6$  throws down, both from neutral and alkaline solutions of Ba, a white precipitate of  $\text{BaSiF}_6$ , which appears only after much agitation and the lapse of some time in dilute solutions; it is perceptibly soluble in HCl and in  $\text{HNO}_3$ . Addition of an equal volume of alcohol renders the precipitation rapid, and so complete that the filtrate remains clear upon addition of  $\text{H}_2\text{SO}_4$ .

85. If baric salts are held on the loop of a platinum wire in the hottest part of *Bunsen's gas flame*, the part of the flame above the sample is colored YELLOWISH-GREEN. With the soluble baric salts, and also with baric carbonate and sulphate, the reaction is immediate, or very soon; but the phosphate, and also the silicates *decomposable by acids*, demand previous moistening of the sample with  $\text{H}_2\text{SO}_4$  or HCl, by which means the Ba may be detected by the flame coloration. The silicates which HCl fails to decompose must be fluxed with  $\text{Na}_2\text{CO}_3$ , when the  $\text{BaCO}_3$  produced will show the reaction. It is characteristic of the yellowish-green baric coloration of the flame that it appears bluish-green when viewed through the green glass. If the sulphates are selected, presence of calcic and strontic sulphates will not interfere with the reaction.—*Fresenius*.

*Characteristic*.—The reactions with  $\text{CaSO}_4$ ,  $\text{K}_2\text{CrO}_4$ , and  $\text{H}_2\text{SiF}_6$ .

86. When O is passed over BaO at a dull red heat, they combine, forming  $\text{BaO}_2$  (baric peroxide), which is an indifferent body, and is decomposed at a bright red heat into BaO and O. Dissolved in  $\text{H}_2\text{O}$  acidulated with HCl, it is converted into  $\text{BaCl}_2$  and  $\text{H}_2\text{O}_2$  hydric peroxide.

87. *Strontium and its compounds*.—The color of Sr is yellow, darker in shade than that of Ca. SrO is a grayish-

white powder or porous mass;  $\text{SrH}_2\text{O}_4$  is also a grayish-white powder; it crystallizes from its solutions in transparent crystals containing 8 at. of water of crystallization.

88. The principal minerals of Sr are the SULPHATE (*celestine*) and the CARBONATE (*strontianite*).

89.  $\text{H}_2\text{SiF}_6$  causes no precipitate in solutions of Sr; even upon addition of an equal volume of alcohol no precipitation takes place, except in very highly concentrated solutions.

90.  $\text{SrCl}_2$  is soluble in alcohol; the solution burns with a *beautiful crimson flame*, which becomes more apparent on stirring the solution.

91. If a small particle of a strontic compound be introduced on the loop of a platinum wire into the flame of a *Bunsen's gas-lamp*, it will impart an *intensely red color* to the flame. As  $\text{SrCl}_2$  gives the most intense coloration of all the strontic compounds, it is advisable, with all the other compounds, first to ignite them in the flame, then moisten with  $\text{HCl}$ , and again to introduce them into the flame. "Viewed through the *blue glass*, the strontic flame appears purple or rose (difference between Sr and Ca, which latter body shows a faint greenish-gray color when treated in this manner); this reaction is the most clearly apparent if the sample moistened with  $\text{HCl}$  is let spirt up into the flame. In presence of Ba the strontic reaction shows only upon the first introduction into the flame of sample moistened with  $\text{HCl}$ ."

*Characteristic.*—The precipitation by  $\text{CaSO}_4$  after the lapse of some time, and the color of the alcohol flame.

92. *Calcium and its compounds.*—The color of Ca is light yellow.  $\text{CaO}$  and  $\text{CaH}_2\text{O}_2$  are white powders.

93. The principal minerals of Ca are the SULPHATE (*gypsum, selenite,  $\text{CaSO}_4, 2\text{H}_2\text{O}$ , anhydrite  $\text{CaSO}_4$* ) the CARBONATE (*chalk, limestone, marble, arragonite, Iceland or calcareous spar*), the double CARBONATE OF LIME and MAGNESIA (*dolomite,  $\text{CaCO}_3, \text{MgCO}_3$* ), and the FLUORIDE (*fluor spar,  $\text{CaF}_2$* ).

94.  $\text{H}_2\text{SiF}_6$  does not precipitate Ca from its solutions.

95. The alcoholic solution of  $\text{CaCl}_2$  or  $\text{Ca}(\text{NO}_3)_2$ , when ignited, burns with a *yellowish-red colored flame*.

96. *Ammonic arsenite* produces, in aqueous solutions of  $\text{CaCl}_2$ , an immediate precipitate of CALCIC ARSENITE. In solutions of  $\text{BaCl}_2$  or  $\text{SrCl}_2$  a precipitate is produced by this reagent only after the lapse of some time. Should this test be resorted to for confirming the presence of Ca,

ammonic salts (if present) must first of all be removed from the solution, because the arsenites which are insoluble in water dissolve in it if ammoniac salts are present.

97. If a small particle of a calcic compound be introduced on the loop of a platinum wire into the melting space of the flame of a *Bunsen's gas-lamp*, it will impart an orange-red color to the outer flame. As  $\text{CaCl}_2$  gives, of all the calcic compounds, the most intense coloration, it is advisable with all the other compounds to moisten them with  $\text{HCl}$  before introducing them into the flame. The coloration appears of a finch-green color when viewed through the green glass, whilst the strontic flame, when viewed through the green glass, appears only of a weak yellow. In the presence of  $\text{Ba}$  the calcic coloration shows only upon the first introduction of the substance into the flame.

*Characteristic.*—The non-formation of a precipitate on the addition of  $\text{CaSO}_4$ , and the formation of a precipitate on the addition of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ , and the coloration of the flame seen through the *green glass*.

98. Before describing the special properties of  $\text{MgO}$  we will give Fresenius's method for the separation and detection of  $\text{BaO}$ ,  $\text{SrO}$ , and  $\text{CaO}$  (par. 99), and also the photochemical method (par. 101).

99. Dissolve the precipitate produced by the group reagent  $(\text{NH}_4)_2\text{CO}_3$ , after it has been well washed in the least possible quantity of  $\text{HCl}$ , and add to a *small portion of the fluid* some solution of  $\text{CaSO}_4$  (not too little); a *precipitate is formed immediately*;\*  $\text{Ba}$  is, and  $\text{Sr}$  and  $\text{Ca}$  may be, present.

100. Evaporate the remainder of the  $\text{HCl}$  solution to dryness, digest the residue with *absolute* alcohol, which dissolves  $\text{SrCl}_2$  and  $\text{CaCl}_2$ , but leaves the greater part of the  $\text{BaCl}_2$  undissolved, filter after having moistened the filter with alcohol, dilute the filtrate with an equal volume of  $\text{H}_2\text{O}$ , mix with a few drops of  $\text{H}_2\text{SiF}_6$ , let the mixture stand several hours to allow time for the trace of  $\text{BaSiF}_6$  to precipitate, then filter and add dilute  $\text{H}_2\text{SO}_4$  to the alcoholic filtrate; the  $\text{Sr}$  and  $\text{Ca}$  will be precipitated as sulphates; filter and wash the precipitate with weak alcohol, then boil the precipitated sulphates in a solution of  $\text{Na}_2\text{CO}_3$ ;

\* If a precipitate is not formed immediately, but only after the lapse of some time, examine the other portion of the solution according to 70; if no precipitate is formed, examine the other portion of the solution according to 69.

$\text{SrCO}_3$  and  $\text{CaCO}_3$  will be formed. Filter, wash the precipitated carbonates with distilled water, then dissolve them in  $\text{HCl}$ , evaporate the solution to dryness, and dissolve the residue in a small quantity of water and examine for  $\text{Sr}$  and  $\text{Ca}$  as directed in par. 71 after the  $\text{Ba}$  has been removed.

101. "The three alkaline earths may be detected in mixtures containing all three of them by the different coloration which they severally impart to the flame. To this end the sample under examination is repeatedly moistened with  $\text{H}_2\text{SO}_4$ , then cautiously dried, and introduced into the fusion zone of the gas flame. After the evaporation of the alkalies that may chance to be present, the baric coloration will make its appearance alone. After this coloration has completely disappeared, and the sample moistened with  $\text{HCl}$  gives on spiriting no longer a flame coloration of a bluish-green tint when viewed through the green glass, the sample is moistened again with  $\text{HCl}$  and tested for  $\text{Ca}$  by viewing it through the green glass when spiriting, for  $\text{Sr}$  by viewing it under the same circumstances through the blue glass."—*Fresenius*.

102. *Magnesium and its compounds*.— $\text{Mg}$  is the color of silver;  $\text{MgO}$  and  $\text{MgH}_2\text{O}_2$  are white powders.

103.  $\text{Mg}$  is found in nature principally in the state of sulphate (*Epsom salts*,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) of carbonate chloride (see par. 43,) and in combination with silicic acid in various proportions, forming the *meerschaum*, *serpentine*, etc.

104.  $\text{NH}_4\text{HO}$  precipitates from aqueous solutions of magnesian salts a portion as  $\text{MgH}_2\text{O}_2$ , the rest of the  $\text{Mg}$  remains in solution as a double salt with the ammoniac one produced.

105. The *fixed alkalies* and the other *alkaline earths* precipitate  $\text{Mg}$  from its solutions as  $\text{MgH}_2\text{O}_2$ , which is soluble in ammoniac salts; their addition, therefore, either before or after the precipitation, prevents or redissolves the precipitate of  $\text{MgH}_2\text{O}_2$ .

106.  $(\text{NH}_4)_3\text{AsO}_4$  produces in neutral or alkaline solutions of  $\text{Mg}$  a precipitate of  $\text{MgNH}_4\text{AsO}_4$ , which is soluble in acetic and other weak acids.

107.  $\text{Na}_2\text{HPO}_4$  produces in concentrated neutral solutions of  $\text{Mg}$  a precipitate of  $\text{MgHPO}_4$ . A magnesian phosphate more soluble in  $\text{H}_2\text{O}$  may be produced by adding, before the  $\text{Na}_2\text{HPO}_4$ ,  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{HO}$ ; in this case the

precipitate is  $\text{MgNH}_4\text{PO}_4$ . Both these magnesian phosphates are soluble in acids.

108. According to the experiments of Dr. Divers,  $(\text{NH}_4)_2\text{CO}_3$ , other ammoniac salts being absent, precipitates Mg completely from its solutions after the lapse of some time, the precipitation commencing to form a few minutes after the addition of the reagent. The precipitate is  $\text{MgCO}_3$ , unless 4 eq. of  $(\text{NH}_4)_2\text{CO}_3$  is added to every one of the magnesian salt; in that case the precipitate is  $\text{MgCO}_3 \cdot (\text{NH}_4)_2\text{CO}_3$ . When  $\text{NH}_4\text{Cl}$  is present, the simple carbonate ( $\text{MgCO}_3$ ) never precipitates, it is always the double carbonate; and when the  $\text{NH}_4\text{Cl}$  is added in the proportion of 2 eq. to every one of the magnesian salt, the precipitate does not begin to form until about a quarter of an hour after the addition of the  $(\text{NH}_4)_2\text{CO}_3$ , and even after the lapse of twenty-four hours the precipitation of the Mg is not complete. The ammoniac magnesian carbonate is more soluble in  $\text{H}_2\text{O}$  than in solutions of  $\text{NH}_4\text{Cl}$  or  $(\text{NH}_4)_2\text{SO}_4$ , and it is almost totally insoluble in solutions of  $(\text{NH}_4)_2\text{CO}_3$ .

109. If magnesian compounds, after being ignited strongly by the blowpipe flame upon a charcoal support, be moistened with a solution of  $\text{Co}(\text{NO}_3)_2$ , and again ignited, the mass assumes, on cooling, a pale *flesh color*.

110. Magnesian salts impart no color to the flame.

*Characteristic.*—The reactions with the soluble phosphates and arseniates, and with  $\text{Co}(\text{NO}_3)_2$ .

111. Answers to the following exercises must be written out.

#### EXERCISES.

19. In what state is Ba, Sr, Ca, and Mg met with in nature?

20. Do you know any baric salt which is insoluble in acids?

21. Mention the similarity and dissimilarity in properties of the metals of this group?

22. Why are you directed to dissolve the precipitated carbonates of the 1st division in acetic acid? Why not dissolve them in  $\text{HCl}$ ?

23. I have some baric sulphate, and I wish to prepare some baric hydrate in solution: how am I to proceed?

24. By what single reagent and in one operation can the absence of Ba and Sr be discovered?

25. Describe the action of Cl upon  $\text{CaH}_2\text{O}_2$  at the com-

mon temperature, at the temperature of boiling water, and at a red heat.

26. How can Ca be detected in the absence of Ba and Sr?

27. Are the oxides of the metals of the alkalies and alkaline earths reducible by H or C?

28. How can Sr be detected in the absence of Ba?

29. Can the presence or absence of Ca be determined as long as Sr remains in solution?

30. If a solution of baric, strontic, or calcic hydrate is exposed to the air it becomes covered with a film: explain the cause of this.

31. Can the presence or absence of Ca and Sr be determined as long as Ba is present in a solution?

32. How is fluoride of silicon prepared? Illustrate by symbols the changes which take place in passing it into water.

33. What occurs when BaO, SrO, CaO, or MgO, is treated with S?

34. Why does the addition of  $\text{NH}_4\text{HO}$  to a solution of a baric, strontic, or calcic salt, to which a solution of  $\text{H}_2\text{O}$  has been previously added, *promote* the formation of the precipitate?

35. Describe as many methods as you are able for distinguishing Ba, Sr, Ca, when they occur in the same solution.

36. What is the action of reagents on solutions of Mg?

37. If you had a solution to examine for the members of the 1st and 2d groups, and from its nature you were certain that baric and strontic compounds were absent, what reagent would you employ to detect and separate the Ca, if present, from Mg and the alkalies?

38. How would you prepare baric carbonate from the sulphate?

39. Supposing you had a solution containing an alkaline carbonate, how could you ascertain qualitatively whether it contained any free alkali?

40. From your knowledge of Berthollet's laws, what would you infer would be the result of adding a solution of  $\text{BaH}_2\text{O}_3$  to an aqueous solution of a magnesian salt?

41. If an oxalate of Ba, Sr, or Ca, was dissolved in an acid, and  $\text{NH}_4\text{HO}$  were added in excess to the acid solution, what would be the effect?

42. Among the impurities contained in coal gas are, as already noticed  $(\text{NH}_4)_2\text{CO}_3$ ,  $(\text{NH}_4)_2\text{S}$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{S}$ . The



gas is frequently made to pass through calcic hydrate: does the hydrate effect any change in these impurities? Illustrate your answer by equations.

43. How is hydric peroxide prepared?

### THIRD GROUP.

ZINCIC OXIDE ( $\text{ZnO}$ ), MANGANOUS OXIDE ( $\text{MnO}$ ), NICKELOUS OXIDE ( $\text{NiO}$ ), COBALTOUS OXIDE ( $\text{CoO}$ ).

Solutions for the reactions:  $\text{ZnSO}_4$ ,  $\text{MnCl}_2$ ,  $\text{NiSO}_4$ ,  $\text{CoSO}_4$ , in water.

112. *Examination for the members of the group.*—When a solution is examined for this group *only*, the group reagent  $(\text{NH}_4)_2\text{S}$  must be added as directed at par. 366, and the precipitate, after being well washed with water containing a little  $(\text{NH}_4)_2\text{S}$ , must be examined, if it is of a *light color*, according to par. 113; if it is of a *black color*, according to par. 114.

113. As the precipitate is of a *light color*, Ni and Co must be absent (J 1, K 1). Examine it for Mn by the blowpipe test; if Mn is *absent*, examine it for Zn by the blowpipe test. *When Mn is present*, dissolve it in as small a quantity of *boiling dilute HCl* as possible;\* boil to expel  $\text{H}_2\text{S}$ ,† then add  $(\text{NH}_4)_2\text{CO}_3$  in excess and boil for some time; the Mn will be precipitated as  $\text{MnCO}_3$  (G 3), whilst Zn, if present, will remain in solution. Filter, and to the filtrate add  $(\text{NH}_4)_2\text{S}$ , when Zn, if present, will be precipitated as sulphide; confirm its presence by dissolving the precipitate, after it has been well washed, in hot dilute  $\text{HNO}_3$ , adding to it a small quantity of a solution of  $\text{Co}(\text{NO}_3)_2$  (not even enough to impart a pink color), then a solution of  $\text{Na}_2\text{CO}_3$  in slight excess; the solution must then be boiled for a minute or two and the precipitate afterwards collected on a filter and washed; the filter with the precipitate is then incinerated on platinum foil. The green color is very

\* In order to use as little acid as possible, pour the boiling acid in small quantities at a time upon the precipitate collected upon the filter. If the precipitate be very large, remove it from the filter into an evaporating dish before adding the acid.

† To ascertain when all the  $\text{H}_2\text{S}$  is expelled, hold a piece of bibulous paper, moistened with a solution of some soluble lead salt, over the boiling liquid; when the lead paper does not alter in color, all the  $\text{H}_2\text{S}$  is expelled.

TABLE III.

BEHAVIOR OF THE THIRD GROUP WITH THE SPECIAL REAGENTS.

MnO.	ZnO.	CoO.	NiO.
G 1. MnS is <i>flesh-colored</i> , but becomes <i>brown</i> on exposure to the air; soluble in the weak acids, as acetic, as well as in the dilute mineral acids.	H 1. ZnS, like the oxide, is white; insoluble in acetic acid, but dissolves in the dilute mineral acids.	J. 1. CoS is <i>black</i> ; insoluble in the dilute mineral acids, as well as in the weaker acids. Soluble in nitro-hydrochloric acid.	K 1. NiS is <i>black</i> ; insoluble in the dilute mineral acids, as well as in the weaker acids. Soluble in nitro-hydrochloric acid.
G 2. The <i>fixed alkalis</i> precipitate from solutions of Mn, $MnH_2O_2$ , which is of a whitish color at first, but speedily becomes blackish-brown on exposure to the air; it is insoluble in an excess of either of the fixed alkalis. The presence of ammoniac salts prevents in a great measure the precipitation.	H 2. The <i>fixed alkalis</i> precipitate from solutions of Zn, $ZnH_2O_2$ , which is white; it is completely soluble in an excess of either of the fixed alkalis, if the alkali is perfectly free from carbonate.	J. 2. The <i>fixed alkalis</i> precipitate, from solutions of Co, <i>blue basic salts</i> , which turn green on exposure to the air; and are converted, upon boiling, into the PALE RED HYDRATE, which is generally discolored, owing to a little $Co_2O_3$ being formed. Each of these precipitates is insoluble in an excess of either of the fixed alkalis.	K 2. The <i>fixed alkalis</i> precipitate from solutions of Ni, $NiH_2O_2$ , in the form of a <i>light green precipitate</i> , which is unalterable in the air, and insoluble in an excess of either of the fixed alkalis.
G 3. $(NH_4)_2CO_3$ produces in solutions of Mn a precipitate of $MnCO_3$ , which is white, and insoluble in an excess of the reagent, especially on boiling.	H 3. $(NH_4)_2CO_3$ produces in solutions of Zn a precipitate of <i>white BASIC CARBONATE OF ZINC</i> , which is easily soluble in an excess of the reagent.	J. 3. $(NH_4)_2CO_3$ produces in solutions of Co a <i>red precipitate of CARBONATE OF COPPER</i> , which is readily soluble in an excess of the reagent, the solution having a red color.	K 3. $(NH_4)_2CO_3$ produces in solutions of Ni a <i>apple-green precipitate of carbonate of nickel</i> , which is readily soluble in an excess of the reagent, the solution having a greenish-blue color.

The alkalis fail to precipitate the members of this group in the presence of non volatile organic matter, such as starch, sugar, tartaric acid, etc.

bright if an excess of cobalt be *avoided*, and is best seen after the gritty residue has been powdered under a glass rod.—*Bloxam*.

114. The precipitate is *black*; all the members of the group must therefore be sought for. Examine a portion of the precipitate for Mn by the blowpipe test. Treat the rest of the precipitate, whether Mn is present or not, with *cold dilute* HCl; NiS and CoS will remain undissolved, whilst MnS and ZnS will dissolve; examine the acid solution according to par. 115, and the undissolved portion according to par. 116.

115. Boil the filtered HCl solution, which may contain Mn and Zn, until all  $H_2S$  is expelled (*see* second note, page 41), then add a solution of one of the *fixed alkalis in excess*; Mn\* will be precipitated, whilst Zn will remain in solution; filter if the alkali has produced any precipitate, and add to the filtrate or to the solution (when it does not require filtering)  $H_2S$ , when Zn, if present, will be precipitated; confirm its presence as directed at par. 113.

116. After having washed the black residue, examine it for Ni and Co in the following way: Expose a small portion of it on a bead of borax to the outer blowpipe flame, in the way directed in par. 152. A blue bead denotes the presence of Co; this is a safe and certain test for Co; consequently, if a blue bead is not produced, Co is absent. If

\* It is almost impossible to prevent a minute quantity of CoS and NiS oxidizing, even if the precipitate is washed most carefully with water containing  $(NH_4)_2S$ ; the oxidized portion of these two bodies will, therefore, be present in the HCl solution, and consequently be precipitated by the fixed alkali; a precipitate may, therefore, be produced by the alkali, when no Mn is present. It will not be necessary to examine this precipitate for Ni and Co, as sufficient will remain undissolved, unless the student has allowed the  $(NH_4)_2S$  precipitate to remain on the filter for a great length of time.

KHO and NaHO solutions very frequently blacken slightly on the addition of  $H_2S$  from their containing small traces of oxides of iron and copper; it is therefore necessary before employing the alkali solution to examine it for these oxides; if one or both of them are present the precipitate produced by  $H_2S$  must be redissolved in a few drops of dilute  $HNO_3$ , and if Cu as well as Fe is present  $H_2S$  must be passed through the solution until it is in excess, the liquid must then be filtered, and the filtrate boiled in an evaporating dish with a few drops of  $HNO_3$  until all the  $H_2S$  is expelled and the Fe has become peroxidized,  $NH_4HO$  is then added in excess, the liquid filtered, and to the filtrate must be added  $(NH_4)_2S$ , which will produce a white precipitate if Zn is present. If the alkali solution does not contain Cu, but only Fe, after the solution of the precipitate in  $HNO_3$ ,  $NH_4HO$  is at once to be added in excess, and the filtrate from the  $NH_4HO$  precipitate tested for Zn with  $(NH_4)_2S$ .

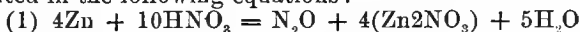
a yellow, and not a blue bead has been formed, which becomes gray and dull in the inner flame, Ni is present. When Co is present, Ni is sought in the following way: The remainder of the precipitate is dissolved in aqua regia, and the acid solution evaporated almost to dryness; a concentrated solution of KCy is then added in excess, and the whole solution must then be boiled for some time, adding a little water from time to time, to replace that which evaporates. To the solution, which must not be filtered even if a precipitate has been formed, is added, when it is cold,  $\text{H}_2\text{SO}_4$  slightly in excess; if in some hours after the acid has been added a precipitate appears, Ni is present; if no precipitate appear, or at least only a crystalline one, which redissolves in water, Ni is absent.

117. Ni may also be detected in the presence of Co by the two following methods. 1st method: The acid solution which contains Co, and which may contain Ni, must be evaporated nearly to dryness,  $\text{KNO}_3$  must then be added in not too small a proportion, and acetic acid to strongly acid reaction, let the mixture stand for at least several hours in a moderately warm place, when Co will separate as nitrate of sesquioxide of cobalt and potash; the Ni may then be readily precipitated from the filtrate by  $\text{NaHO}$  or  $(\text{NH}_4)_2\text{S}$ . 2d method: Saturate with Cl the very dilute solution of the two metals in  $\text{HCl}$ , having the acid slightly in excess; add  $\text{BaCO}_3$  in excess, and let the fluid stand twenty-four hours. The Co is entirely precipitated in this process as black sesquioxide, whilst the Ni remains in solution, and may, after the removal of the Ba by  $\text{H}_2\text{SO}_4$ , be precipitated by solution of  $\text{NaHO}$ .

118. *The following precautions are to be attended to in the analysis of this group:* When Mn is present, care must be taken to expel all the  $\text{H}_2\text{S}$  from the  $\text{HCl}$  solution, before  $(\text{NH}_4)_2\text{CO}_3$  is added to separate the Mn from the Zn. Before adding  $\text{H}_2\text{SO}_4$  to the KCy solution, it will be better to add a little water, in order to prevent any  $\text{K}_2\text{SO}_4$  from crystallizing out, which might mislead the student as regards Ni. On adding  $\text{NaHO}$  to the  $\text{HCl}$  solution, which may contain the Zn and Mn and small traces of Ni and Co, from the partial oxidation of their sulphides, a small precipitate will frequently be formed, if only Zn be present. This is occasioned by the caustic alkali having absorbed some  $\text{CO}_2$  from the air, and become partially converted into carbonate, which causes a partial precipitation of the Zn.

PROPERTIES OF THE METALS, THE OXIDES, THE SULPHIDES, THE CHLORIDES, THE NITRATES, THE SULPHATES, OF THIS GROUP.

119. *The metals.*—Zn melts at  $412^{\circ}\text{C.}$ , and at a bright red heat volatilizes; the other three metals are almost as infusible as Fe. In damp air Mn gradually crumbles down to a brown oxide, Zn is tarnished, the other two are less affected by it than Fe; they all combine with O on exposure to air or O, at a red heat, the combination with Zn being attended with flame. Mn decomposes water slowly at common temperatures; the other three decompose it at a red heat, with disengagement of H. They dissolve in dilute  $\text{H}_2\text{SO}_4$  and in  $\text{HCl}$ , H being evolved, and salts of the metals formed.  $\text{HNO}_3$  oxidizes and dissolves them, a nitrate of the metal being formed. The gaseous compound formed in the case of Co and Ni is  $\text{NO}_2$ ;  $\text{N}_2\text{O}$  is one of the gaseous products when Zn is acted upon by dilute acid. The gaseous body formed depends in this, as in other cases, on the strength of the acid and the temperature, for if Zn be acted upon by undilute  $\text{HNO}_3$ ,  $\text{NH}_3$  is one of the products. These two reactions are represented in the following equations:—



If an excess of acid be employed, it, or a portion of it, combines, of course, with the  $\text{NH}_3$  formed in the second reaction. Zn decomposes  $\text{CO}_2$  at a red heat; it dissolves in boiling  $\text{KHO}$ , H being evolved; thus,  $\text{Zn} + 2\text{KHO} = \text{K}_2\text{O}, \text{ZnO} + \text{H}_2$ .

Co and Ni are magnetic; the Ni loses this property almost entirely if heated to a point exceeding  $332^{\circ}\text{C.}$ , but recovers its magnetic power on cooling.

120. *The oxides* may be obtained by igniting the hydrates or carbonates out of contact of the air; they are non-volatile, and are not decomposed by heat alone; they may be reduced to the metallic state by ignition with C, or, with the exception of Mn, on being heated in a current of H or CO. On being heated with  $\text{NH}_4\text{Cl}$ , CoO and NiO are reduced to the metallic state, but ZnO and MnO are left by it in the state of chlorides. On being heated in contact with air, ZnO and NiO suffer no change, but MnO and CoO are converted into  $\text{Mn}_3\text{O}_4$  and  $\text{Co}_3\text{O}_4$ . ZnO, CoO, and NiO, on being heated with S, are converted into sulphides,  $\text{SO}_2$  being evolved; in the case of MnO an oxysulphide is formed. Heated in a current of Cl, they are converted

into chlorides, O being evolved. *The hydrates* are obtained by adding to solutions of their salts one of the fixed alkalies, as shown in Table III.  $\text{ZnO}$  and  $\text{ZnH}_2\text{O}_2$  are *white*;  $\text{ZnO}$ , when heated, turns *lemon-yellow*, and on cooling turns *white* again;  $\text{MnO}$  is *grayish-green*,  $\text{MnH}_2\text{O}_2$  is *white*; both absorb O from the air, and become converted into *brown*  $\text{Mn}_2\text{O}_3\cdot\text{H}_2\text{O}$ .  $\text{NiO}$  is *grayish-green*;  $\text{NiH}_2\text{O}_2$  is *green*;  $\text{CoO}$  is an *olive-green*;  $\text{CoH}_2\text{O}_2$  is *pale red*. These oxides and hydrates are in the form of powders, and are insoluble in  $\text{H}_2\text{O}$ , but dissolve readily in  $\text{HNO}_3$ ,  $\text{HCl}$ , and  $\text{H}_2\text{SO}_4$ .  $\text{ZnO}$  and its hydrate are soluble in the alkalies,  $\text{CoO}$  and  $\text{NiO}$  and their hydrates in the volatile alkali, and  $\text{MnO}$  and its hydrate in  $\text{NH}_4\text{Cl}$ . If Cl is passed through  $\text{H}_2\text{O}$  in which  $\text{MnO}$ ,  $\text{NiO}$ , or  $\text{CoO}$ , or their hydrates, are suspended, a part of the metal is precipitated in the state of  $\text{M}_2\text{H}_6\text{O}_6$ , and the remainder remains in solution as  $\text{MCl}_2$ , if the liquid, in which the oxides or the hydrates are suspended, is strongly *alkaline* the *whole* of the Co and Ni are converted into the hydrates of the sesquioxides  $\text{Co}_2\text{H}_6\text{O}_6$  and  $\text{Ni}_2\text{H}_6\text{O}_6$ , and the Mn is converted into the hydrated  $\text{MnH}_4\text{O}_3$ .

121. *The sulphides* are obtained in the *hydrated* state by adding to a solution of their salts an alkaline sulphide, or by passing into their alkaline solutions  $\text{H}_2\text{S}$ ; their *color* and their solubility in acids are noticed in Table III. They are insoluble in  $\text{H}_2\text{O}$  in the alkalies and alkaline sulphides, with the exception of  $\text{NiS}$ , which, under certain circumstances, dissolves to a slight extent in the alkaline sulphides, imparting thereby to the solution a brownish color.  $\text{H}_2\text{S}$  causes no precipitate in solutions of these metals containing free mineral acids, but it precipitates completely Zn from the solution of the acetate, even if free acetic acid is present. In neutral solutions  $\text{H}_2\text{S}$  does not completely precipitate the metals as hydrated sulphides, the solutions of zincic, cobaltous, and nickelous acetates excepted. They all oxidize more or less on exposure to air.  $\text{SO}_2$  converts  $\text{MnS}$  and  $\text{ZnS}$  into hyposulphites, but it dissolves only sparingly the other two. Heated out of contact with air, they are converted into anhydrous sulphides,  $\text{H}_2\text{O}$  being expelled. In the anhydrous state  $\text{ZnS}$  is of a yellowish color,  $\text{MnS}$  is green,  $\text{NiS}$  bronze yellow with metallic lustre,  $\text{CoS}$  is gray with metallic lustre. In the anhydrous as well as in the hydrated state they are decomposed more or less readily when heated in a current of Cl, metallic chlorides being formed, and chloride of sul-

phur\* evolved. Roasted in air, they are converted into oxides with evolution of  $\text{SO}_2$ . The hydrated sulphide of Mn precipitates Co as  $\text{CoS}$  from solutions of its salts, and the hydrated sulphides of Mn and Co precipitate Ni from the solutions of its salts, and Fe from  $\text{Fe}_2\text{Cl}_6$ , Pb from  $\text{Pb}(\bar{\text{A}})_2$ , Cu from  $\text{CuSO}_4$ , and Ag from  $\text{AgNO}_3$ , as sulphides.

122. The *chlorides* may be obtained by dissolving the metals, the anhydrous or hydrated oxides or carbonates in  $\text{HCl}$ , or by dissolving in this acid by the aid of heat any of the higher oxides of Mn, Co, or Ni; in these latter cases  $\text{Cl}$  is evolved. On evaporating the solutions obtained by any of these modes, the salts are obtained crystallized and hydrated, thus:  $\text{ZnCl}_2 \cdot \text{H}_2\text{O}$ ,†  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 9\text{H}_2\text{O}$ . They may be obtained in the anhydrous state by igniting the hydrates, or by heating the metals in a current of  $\text{Cl}$ ; in the anhydrous state they all attract moisture from the air, but the first two deliquesce in the hydrated state.  $\text{MnCl}_2$  and  $\text{ZnCl}_2$  melt at a dull red heat; at higher temperatures they sublime, and the latter can be distilled; the other two may sublime without first fusing; if ignited in the air above the fusing point  $\text{MnCl}_2$ , if the ignition is protracted, becomes converted into oxide, and the others lose more or less  $\text{Cl}$ , a corresponding quantity of oxide being formed. Heated in  $\text{PH}_3$ , they are converted into phosphides,  $\text{HCl}$  being evolved; and with the exception of  $\text{MnCl}_2$  they are reduced to the *metallic* state when heated to redness in a current of  $\text{H}$ . If  $\text{Cl}$  is passed through solutions of  $\text{MnCl}_2$  and  $\text{CoCl}_2$ , they are converted into  $\text{Mn}_2\text{Cl}_6$  and  $\text{Co}_2\text{Cl}_6$ , and on the subsequent addition of  $\text{BaCO}_3$ ,  $\text{Mn}_2\text{O}_3$  and  $\text{Co}_2\text{O}_3$  are precipitated.

123. The *nitrates* may be obtained by dissolving the metals in  $\text{HNO}_3$ , or the anhydrous or hydrated oxides or the carbonates in the acid diluted; they are soluble in  $\text{H}_2\text{O}$ , and on evaporating their aqueous solutions crystallized hydrated salts are obtained; they are decomposed on ignition, a higher oxide of Mn, Ni, and Co, than the monoxide being left.

124. The *sulphates* may be obtained by dissolving the metals, the anhydrous or hydrated oxides, or the carbon-

\* There are two chlorides of sulphur,  $\text{S}_2\text{Cl}_2$  and  $\text{SCl}_2$ ; they are decomposed by water into  $\text{SO}_2$ ,  $\text{HCl}$ , and  $\text{S}$ .

†  $\text{ZnCl}_2$  in solution, under the name of Burnett's Disinfecting Fluid, has been extensively used as an antiseptic and as a preservative of wood and vegetable fibre.

ates in dilute  $\text{H}_2\text{SO}_4$ ; or by heating the higher oxides of Mn, Ni, Co, in undilute acid, and  $\text{ZnSO}_4$  may be prepared by gently roasting in the air zinc blende. They are soluble in  $\text{H}_2\text{O}$ , and crystallize from their aqueous solutions on evaporation,  $\text{MnSO}_4$  with 5 atoms,\* and the other three with 7 atoms, of  $\text{H}_2\text{O}$ . On being heated the water is expelled, and they are left in the anhydrous state; they bear a moderately strong red heat without decomposing, but at a bright red heat they are decomposed, the metals being left in the state of oxides, higher oxides than the monoxides in the case of Mn, Ni, and Co.

125. *The general characters of the salts of this group.*—The zincic salts, in the anhydrous and hydrated states, are *white*; the manganous salts are *white* or *red*; most of the nickelous salts are *yellow* in the anhydrous, and *green* in the hydrated state, their *solutions* are of a *light green* color; the cobaltous salts are *red* in their hydrated, and mostly *blue* in their anhydrous state, their *solutions*, even when much diluted, have a delicate *rose tint*; the *red* solution of  $\text{CoCl}_2$  on evaporation turns *blue*, or on the addition of strong mineral acids to its solutions. The neutral salts of these metals, soluble in water, are decomposed by heat, the sulphates being the least decomposable; the manganous soluble neutral salts are *neutral*, and the soluble neutral salts of the other three metals are *acid*, to litmus paper. Zincic and manganous compounds, which are insoluble in  $\text{H}_2\text{O}$ , dissolve in  $\text{HCl}$ ; and *most* of the nickelous and cobaltous compounds, which are insoluble in  $\text{H}_2\text{O}$ , are soluble in  $\text{HCl}$ .  $\text{BaCO}_3$ , or  $\text{CaCO}_3$  does not precipitate the oxides from aqueous solutions of the salts upon digestion in the cold, *with the exception of the sulphates*; but if the solution has been treated with Cl or Br, Mn and Co are precipitated from their salts by these carbonates, as  $\text{Mn}_2\text{O}_3$  and  $\text{Co}_2\text{O}_3$ . A solution of  $\text{Na}_2\text{CO}_3$  precipitates from solutions of the *normal* salts of Co, Ni, and Zn, as it does

\*  $\text{MnSO}_4$  crystallizes below  $42^\circ$  with 7 ats. of  $\text{H}_2\text{O}$ , and between  $45^\circ$  and  $68^\circ$  with 5 atoms, and between  $68^\circ$  and  $86^\circ$  with 4 atoms. The sulphates of Mg, Zn, Mn, Co, Ni, and Fe are isomorphous; they usually crystallize with 7 ats.  $\text{H}_2\text{O}$ , but under certain conditions with 5, and cupric sulphate, which belongs to the group, never contains more than 5; they sometimes crystallize with 4, and sometimes even with 2. These sulphates, which are frequently termed magnesian sulphates, retain 1 at.  $\text{H}_2\text{O}$  with considerable force, and it can be replaced by an anhydrous sulphate, as  $\text{K}_2\text{SO}_4$ ; these double sulphates, even the double cupric sulphate, always crystallize with 6 ats.  $\text{H}_2\text{O}$ . This atom of water was called by Graham constitutional water.



also from similar salts of Mg and Cu, not a normal, but a basic, carbonate. The members of this group are distinguished from those of the preceding by the insolubility of their oxides and sulphides in  $H_2O$ , and from those of the next group by their behavior with  $NH_4HO$ .\*

REMARKS ON THE INDIVIDUAL MEMBERS OF THE GROUP, WITH  
ADDITIONAL SPECIAL TESTS.

126. *Mn and its compounds*.—Mn is grayish-white, very brittle, and melts only at the strongest heat of a blast furnace.

127. The most important and most valuable ore of Mn is the peroxide ( $MnO_2$ ); it is employed for obtaining Cl from HCl.

128.  $NH_4HO$  precipitates from solutions of manganous salts part of the Mn as  $MnH_2O_2$ , which an excess of the reagent does not redissolve; but  $NH_4HO$  produces no precipitate in the presence of  $NH_4Cl$ , or any ammoniac salt the acid of which forms no insoluble salt with Mn. An ammoniac solution of Mn rapidly attracts O from the air, one of the higher oxides of Mn being formed, which is insoluble in  $NH_4HO$ , and therefore precipitates as quickly as it is formed, and in brownish flocks.

129. If a few drops of a fluid containing a manganous compound, and free from Cl, are sprinkled on  $PbO_2$  or  $Pb_3O_4$ , and  $HNO_3$  free from Cl is then added, and the mixture boiled and allowed to settle, the  $Mn(NO_3)_3$  formed imparts a *purple-red* color to the fluid.

130. The smallest quantity of Mn can be detected in any of its compounds, by fusing them, in conjunction with  $Na_2CO_3$  and a small quantity of  $KNO_3$ , upon platinum foil or wire, in the outer blowpipe flame; sodic manganate ( $Na_2MnO_4$ ), which is of a bluish-green color, being produced,† which, on being dissolved in  $H_2O$ , yields a *green* solution, turning *red* on the addition of acetic acid, and

\* Cobaltous and nickelous oxalates are nearly insoluble in water and in a solution of oxalic acid, but they are soluble in  $NH_4HO$ ; on exposing to the air an ammoniac solution of the two oxalates for several days, the nickelous oxalate is deposited, whilst the cobaltous oxalate remains in solution.

† The manganates and permanganates, especially the latter, are employed as oxidizing and disinfecting agents; under the name of *Condy's fluid*, they are largely used for these purposes.

Before making the blowpipe experiments, consult the pars. under the head "Blowpipe" in Part III.

often afterwards becoming colorless, with separation of brown flocculi. "This method fails to detect manganese in limestone rocks, on account of the insolubility of the lime salt in  $\text{Na}_2\text{CO}_3$  and  $\text{KNO}_3$ ; but if, along with the two reagents just mentioned, a little borax be added, so as to attack and dissolve a portion of the mass, the well-known greenish-blue enamel is quickly produced."—*Chapman*.

*Characteristic*.—The reactions with  $(\text{NH}_4)_2\text{S}$ ,  $\text{PbO}_2$  and the blowpipe test.

131. Five other oxides of Mn are known:  $\text{Mn}_2\text{O}_3$ , feebly basic, is found in nature in the anhydrous and hydrated states; it may be formed by exposing  $\text{MnO}$  or  $\text{MnH}_2\text{O}_2$  to air, or by passing  $\text{Cl}$ , not to saturation, through  $\text{H}_2\text{O}$  in which  $\text{MnH}_2\text{O}_2$  or  $\text{MnCO}_3$  is suspended.  $\text{Mn}_3\text{O}_4$  is found in nature; the other oxides of Mn are converted into this one by igniting them in the air.  $\text{MnO}_2$  is found in nature in the anhydrous and the hydrated state; this and the previous oxide are indifferent bodies;  $\text{MnO}_2$  is left in the hydrated state when  $\text{Mn}_3\text{O}_4$  is treated with  $\text{HNO}_3$ . The two next are acid bodies; they cannot exist except in combination, with H, or a metal; the general formula of their salts is  $\text{M}_2\text{MnO}_4$ ,  $\text{M}_2\text{Mn}_2\text{O}_8$ . The first are termed manganates and the latter permanganates; they are formed by fusing  $\text{MnO}_2$  with  $\text{KHO}$ . Each of these oxides is converted into  $\text{MnCl}_2$ , with evolution of  $\text{Cl}$  on being heated with  $\text{HCl}$ .

132. *Zn and its compounds*.—Zn is a hard, bluish-white metal; it is rather brittle at ordinary temperatures, but between  $94^\circ$  and  $149^\circ \text{C}$ ., it possesses considerable ductility and malleability; at a little higher temperature it again becomes so brittle that it may be powdered in a mortar. Zn is a constituent of several alloys; brass, pinchbeck, muntz or yellow metal, and *hard solder* for brass are alloys of Cu and Zn; other alloys we shall notice under the other metals.

133. The principal minerals of Zn are the anhydrous CARBONATE (calamine,  $\text{ZnCO}_3$ ) and the SULPHIDE (Zinc blende  $\text{ZnS}$ ).

134. When compounds of Zn mixed with  $\text{Na}_2\text{CO}_3$  are subjected upon a charcoal support to the inner blowpipe flame, Zn is produced, which volatilizes, and, on passing through the oxidizing flame, becomes again converted into oxide. The charcoal support becomes incrustated with this oxide, which is of a yellow color while hot, and turns white on cooling.

135. If a compound of Zn be moistened with  $\text{Co}(\text{NO}_3)_2$  and exposed on charcoal to the outer blowpipe flame, a mass of a beautiful green color will be produced; the color is best seen when the mass has become cold.

136. (a) "*Reduction-film* black, in the thin parts brown.

(b) "*Oxide-film* white, and therefore invisible. To test it, a square centimètre of filter-paper moistened with  $\text{HNO}_3$  is rubbed over the surface and then rolled up on two rings on fine platinum wire, three millimètres in diameter, and burnt. If the paper is burnt in the upper oxidizing flame at as low a temperature as possible, the ash forms a small solid mass about a square millimètre in area, which can be ignited without fusion, and becomes yellow on gently heating, and appearing white on cooling. If this be moistened with a few milligrammes of very dilute  $\text{Co}(\text{NO}_3)_2$  solution and ignited, it appears of a beautiful green color on cooling; the same reaction can be effected with the metallic-film."—*Bunsen*.

*Characteristic*.—The reactions with  $\text{KHO}$ ,  $(\text{NH}_4)_2\text{S}$  and the blowpipe test.

137. Zn forms only one oxide, so far at least as is at present known.

138. *Ni and its compounds*.—Ni is a brilliant, silver-white, hard but ductile metal; it surpasses Fe in tenacity. It may be obtained pure by heating the oxalate intensely in a crucible with a luted cover. The principal ore of Ni is copper-nickel ( $\text{NiAs}$ ).  $\text{NiO}$  yields insoluble compounds with  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{BaO}$ ,  $\text{SrO}$ , and several other bases; some of them are decomposed by frequent washings with boiling water. German silver, packfong, and tutenag (a Chinese alloy), are alloys of Ni, Zn, and Cu.

139.  $\text{NH}_4\text{HO}$ , added in small quantity to solutions of Ni, produces in them a trifling greenish turbidity; upon further addition of the reagent, this redissolves readily to a blue fluid, containing a compound of oxide of nickel and ammonia.

140.  $\text{KC}_y$  throws down from solutions of Ni a yellowish-green precipitate of  $\text{NiC}_y$ , which redissolves in an excess of the precipitant as  $\text{NiC}_y$ ,  $2\text{KC}_y$ ; the solution is brownish-yellow, on the addition of  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  to this solution  $\text{NiC}_y$  is reprecipitated, whilst the  $\text{KC}_y$  is decomposed,  $\text{HC}_y$  being evolved; the  $\text{NiC}_y$  is very difficultly soluble in an excess of either of the acids in the cold, but more readily upon boiling.

141.  $\text{KNO}_3$ , used in conjunction with acetic acid, fails to precipitate Ni even in concentrated solutions.

142. In the exterior flame of the blowpipe, nickel compounds impart to beads of borax a reddish-yellow tint; the color fades upon cooling, and finally disappears almost entirely. If exposed with borax to the inner flame, the bead becomes gray; if a minute fragment of  $\text{KNO}_3$  be added to the bead after exposure to the inner flame, and it is then fused in the outer flame, it acquires a rich purple color.

143. "*Reduction on charcoal splinter.*—On pulverizing the charcoal white, lustrous, ductile, metallic particles are obtained, forming a brush on the magnetized blade. The metal dissolved in  $\text{HNO}_3$  on paper gives a green solution, which on moistening with soda, exposure to bromine vapor, and subsequent addition of soda, gives a brownish-black spot of  $\text{Ni}_2\text{O}_3$ . The ash of the paper, from which the excess of soda has been washed out, can be used for the borax-bead test."—*Bunsen*.

144. *Borax-bead.*—"Oxidizing flame grayish-brown, or dirty violet. Upper reducing flame gray, from reduced Ni, which often collects to a spongy mass of metal, rendering the bead colorless."—*Bunsen*.

*Characteristic.*—The reactions with  $\text{NH}_4\text{HO}$ ,  $\text{KC}_y$ , and the blowpipe test.

145. There is one other oxide of Ni known, viz.  $\text{Ni}_2\text{O}_3$ ; it forms no salts, and is converted on being heated with acids into nickelous salts; it may be obtained by digesting  $\text{NiH}_2\text{O}_2$  with  $\text{Cl}$ , or with an alkaline hypochlorate.

146. *Co and its compounds.*—Co is hard and of a reddish-gray color. The principal minerals of this metal are the TIN-WHITE COBALT, or SMALTINE ( $\text{CoAs}_2$ ), and the bright white cobalt, or cobalt glance ( $\text{CoS}_2$ ,  $\text{CoAs}_2$ ).

147. " $\text{CoO}$  combines with bases as well as with acids. If fused with  $\text{KHO}$  it forms a *blue* compound, which is decomposed by the free addition of  $\text{H}_2\text{O}$ ; when heated with  $\text{Mg}(\text{NO}_3)_2$  a pale *pink* residue is obtained, a combination of  $\text{MgO}$  and  $\text{CoO}$ ; with  $\text{Al}_2\text{O}_3$ , it forms the blue pigment known as Thénard's blue, and with  $\text{ZnO}$  the compound known as Rimner's green." This, and other oxides of Co, on being treated with ammonia, unite with it forming ammonio-cobalt bases of complex constitution. Characters traced on paper with a dilute solution of  $\text{CoCl}_2$ , are invisible in the cold, but become blue by heat, and again fade in the cold as the hygroscopic moisture of the paper is restored.

The chief use of cobalt in the arts is in the production of smalts (powdered blue glass), Thénard's blue, Rimner's green, and other pigments.

148.  $\text{NH}_4\text{HO}$  produces in solutions of cobaltous salts the same precipitate as the fixed alkalis do; but the precipitate is soluble in an excess of  $\text{NH}_4\text{HO}$ , the ammoniac solution having a reddish-brown color: the fixed alkalis produce no precipitate, or at least a very slight one, in the ammoniac solution.  $\text{NH}_4\text{HO}$  causes no precipitate, if  $\text{NH}_4\text{Cl}$  is present.

149.  $\text{KC}_y$  precipitates from *acid* solutions of cobalt salts a brownish-white cobaltous cyanide  $\text{CoC}_y$ , dissolving easily in an excess of the precipitant, from which solution the  $\text{CoC}_y$  cannot be again precipitated by acids, as it exists now in the form of potassic cobalti-cyanide,  $\text{K}_3\text{Co}'''_2\text{C}_{12}$ .



150. "If the solution contains Ni, as well as Co, the addition of  $\text{HCl}$  to the solution of the cyanides produces a greenish precipitate, which always contains the whole of the Ni, and under particular circumstances all the Co—that is, when these two metals are in the proportion of 3 eq. of Ni to 2 eq. of Co. The precipitate consists then of nickelous cobalti-cyanide,  $\text{Ni}_3\text{Co}_2\text{C}_{12}$ . In case of a larger proportion of Ni, the precipitate is a mixture of  $\text{NiC}_y$  and the former compound; but if the proportion of Ni is smaller, a part of the Co remains in solution as  $\text{K}_3\text{Co}_2\text{C}_{12}$ ."—Will.

151. Co may be completely precipitated from its neutral solutions by  $\text{KNO}_3$  as an orange-yellow body ( $\text{Co}_2\text{O}_3$ ,  $2\text{N}_2\text{O}_3$ ,  $6(\text{KNO}_2)2\text{H}_2\text{O}$ ). Before adding the  $\text{KNO}_2$  the solution must be evaporated to a small bulk, and neutralized by  $\text{KHO}$  if it contains excess of acid; acetic acid must be added after the  $\text{KNO}_2$  to strongly acid reaction, and the mixture is left to stand for some time. This reaction separates Co from Ni, Mn, Zn, and many other metals.

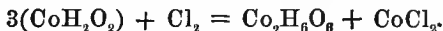
152. The compounds of Co fused with borax in the loop of a platinum wire, in either flame of the blowpipe, produce a beautiful blue glass, which is a very delicate and characteristic test for Co. The cobalt compound must be used in very small proportion.

153. *Reduction on charcoal splinter*.—"By pulverizing the charcoal, white, ductile, lustrous, metallic particles are obtained, which form a brush on the magnetic blade. The metal, rubbed off on to paper, gives a red solution when moistened with  $\text{HNO}_3$ ; this yields a green color on addi-

tion of  $\text{HCl}$  and drying, which disappears again on moistening. The paper moistened with soda, brought into bromine-vapor and again moistened with soda, yields a brownish-black spot of  $\text{Co}_3\text{O}_4$ . This reaction is plainly seen with a few tenths of a milligramme of metal. The paper can also be used, after washing out the soda and burning, for the coloration of the borax bead."—*Bunsen*.

*Characteristic.*—Reactions with  $\text{KHO}$ ,  $\text{NH}_4\text{HO}$ ,  $\text{KCy}$ ,  $\text{KNO}_2$ , and the blowpipe tests.

154.  $\text{Co}$  unites with  $\text{O}$  in several other proportions, the oxide  $\text{Co}_2\text{O}_3$  is formed as hydrate by suspending  $\text{CoH}_2\text{O}_2$  in  $\text{H}_2\text{O}$ , and passing into it  $\text{Cl}$ ,  $\text{Co}_2\text{H}_6\text{O}_6$  is precipitated as a black powder, whilst  $\text{CoCl}_2$  remains in solution; thus:—



If the oxide is suspended in solution of  $\text{KHO}$  it is all converted into  $\text{Co}_2\text{H}_6\text{O}_6$ . The other oxides of  $\text{Co}$  are formed by a combination of these two in different proportions.  $\text{Co}_3\text{O}_4$  is formed by heating  $\text{CoO}$  to dull redness in the air, or by igniting  $\text{Co}_2\text{O}_3$ .  $\text{Co}_2\text{O}_3$  is converted into cobaltous salts on being heated with acids.

155. Answers to the following exercises must be written out:—

#### EXERCISES.

44. In what state do  $\text{Co}$ ,  $\text{Ni}$ ,  $\text{Mn}$ , and  $\text{Zn}$ , occur in nature?

45. If I desired to precipitate manganese completely from a solution by ammonia, in what state must I take care to have it in the solution?

46. A mixture of  $\text{MnO}$ ,  $\text{NiO}$ , and  $\text{CoO}$ , is placed in a tube, a current of dry  $\text{HCl}$  gas is passed over it, and it is at the same time exposed to a moderate red heat; the transmission of the gas and the ignition are continued until the formation of  $\text{H}_2\text{O}$  ceases; what change has the  $\text{HCl}$  effected? Dry  $\text{H}$  is then passed over it, and a stronger heat applied until a slight cloud only is perceptible upon approaching a glass rod, moistened with ammonia, to the mouth of the tube—what changes has the  $\text{H}$  effected?

47. If you had to manufacture zinc sulphate, what substance or substances would you employ; give the composition of crystallized salt.

48. A mixture of  $\text{ZnO}$ ,  $\text{NiO}$ , and  $\text{CoO}$  is mixed with sugar, and the mixture is then placed in a covered crucible, which is then heated gradually, until it attains the very

highest degree obtainable in a wind furnace, at which temperature it is kept for some time. State what changes the oxides have undergone, and what remains in the crucible?

49. When any of the oxides of manganese are ignited in contact with the air, in what state are they left?

50. A mixture of  $\text{MnO}$ ,  $\text{NiO}$ ,  $\text{ZnO}$ , and  $\text{CoO}$ , is placed on a piece of porcelain and inserted in a tube; a stream of  $\text{H}_2\text{S}$  is passed through the tube, and the tube is then heated to dull redness; after allowing the substance to cool in the tube in an atmosphere of the  $\text{H}_2\text{S}$ , it is digested for some time in cold dilute  $\text{HCl}$ —what occurs? To the filtered  $\text{HCl}$  solution is added sodic acetate in excess, and  $\text{H}_2\text{S}$  is then passed through the solution. What changes take place, and why is the sodic acetate added?

51. Name the principal ore of manganese, and state for what it is chiefly employed; illustrate your answer by an equation.

52. Illustrate by means of equations the changes which take place in a solution containing a salt of nickel and one of cobalt (say  $\text{NiSO}_4$  and  $\text{CoCl}_2$ ), when a solution of  $\text{KCy}$  is added in excess, and the solution afterwards slightly acidulated with  $\text{H}_2\text{SO}_4$ : (1) When the metals are in the proportion of 3 atoms of  $\text{Ni}$  to 2 of  $\text{Co}$ ; (2) When they are in the proportion of 6 of  $\text{Ni}$  to 2 of  $\text{Co}$ ; (3) When they are in the proportion of 3 of  $\text{Ni}$  to 6 of  $\text{Co}$ .

53. I treat a mixed precipitate of the sulphides of  $\text{Mn}$ ,  $\text{Ni}$ ,  $\text{Zn}$ , and  $\text{Co}$ , with acetic acid. What change (if any) takes place?

54. A colorless solution is given you to examine for the members of the first, second, and third groups. State what members of these groups are probably absent.

55. Describe the chief properties and the applications of  $\text{Ni}$  and  $\text{Co}$ .

56. Describe the changes which would take place on roasting  $\text{ZnS}$  at a gentle heat in contact with the air, and exposing the roasted mass to a red heat.

57. Describe as many methods as possible for separating the members of this group by the aid of Table III. and the text.

58. How is  $\text{NH}_4\text{HS}$  and  $(\text{NH}_4)_3\text{S}$  prepared, and describe by means of equations the changes which take place on treating neutral solutions of  $\text{MnCl}_2$  with these sulphides?

59. I mix  $\text{ZnO}$ , obtained by roasting blende or calamine, with one-half its weight of charcoal, coke, or anthracite in

powder. The mixture is introduced into a crucible, in the bottom of which is an opening into which an iron pipe has been accurately fitted; the upper end of the tube reaches nearly to the top of the crucible, the lower end projects some distance out of it. After the introduction of the mixture the crucible is covered with a lid, made air-tight by means of fire-clay; the crucible is then placed in a furnace, in the sole of which there is a hole for the lower end of the iron tube to pass through; the crucible is exposed in the furnace to a strong heat—what occurs?

60. How is potassic nitrite prepared?

61. How is chlorine prepared?

62. Describe the method for the preparation of microcosmic salt, and give its formula.

63. Describe by means of equations the two methods given in Part III. for the preparation of potassic cyanide.

#### FOURTH GROUP.

ALUMINIC OXIDE ( $\text{Al}_2\text{O}_3$ ), CHROMIC OXIDE ( $\text{Cr}_2\text{O}_3$ ), FERRIC OXIDE ( $\text{Fe}_2\text{O}_3$ ), FERROUS OXIDE ( $\text{FeO}$ ).

ALUMINIC, CHROMIC, AND IRON PHOSPHATES; THE PHOSPHATES OF THE ALKALINE EARTHS. BARIUM, STRONTIUM, AND CALCIUM OXALATES.\*

URANIC OXIDE ( $\text{U}_3\text{O}_8$ ). TITANIC OXIDE ( $\text{TiO}_2$ ).

*Solutions for reactions.*— $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{Cr}_2\text{Cl}_6$ ,  $\text{Fe}_2\text{Cl}_6$ ,  $\text{FeSO}_4$  in  $\text{H}_2\text{O}$ .

156. *Examination for the members of the group.*—When a solution is examined for the members of this group only, the *group reagent*,  $\text{NH}_4\text{OH}$ , must be added, as directed at par. 363, and the precipitate, after being thoroughly washed

\* The phosphates and oxalates do not engage the attention of the student as he passes through the basic groups; he has therefore only to deal with the substances given in Table IV. It is not until he has had some practice in examining both for acids and bases that the insoluble salts which are precipitated along with the oxides of this group are included in the course; the precipitate is then examined according to Table V. Manganous phosphate is also precipitated by  $\text{NH}_4\text{OH}$ , although it has not been included in the list of phosphates precipitated by that reagent.

Uranic and titanio oxides are classed amongst the rare substances; they do not therefore form a part of the group, and are therefore not included in Tables IV. or V.



with boiling water, must be examined for the *members of this group* and also for Mn, as it is precipitated in greater or less quantity by  $\text{NH}_4\text{HO}$ ; the cause of its precipitation is explained in par. 128. We shall describe three methods for the examination of this group; the first or second is probably the best when Fe or Mn is present. Separate portions of the *original* solution must be tested for Fe both in the ferrous and ferric states; for  $\text{Fe}''$  according to par. 177, for  $\text{Fe}'''$  according to par. 176 or 179, the latter if Cu is in the solution. A small portion of the precipitate must be examined for Mn by the blowpipe test (par. 130).

157. *1st Method.*—Fuse\* the precipitate with equal parts of  $\text{Na}_2\text{CO}_3$  and  $\text{NaNO}_3$ † or  $\text{KNO}_3$  in a platinum crucible; after the fusion, allow the mass to cool, and then boil it with water and filter. If much Cr is present the filtrate will have a *yellow color*; add to the filtrate acetic acid in excess, then  $\text{Pb}(\bar{\text{A}})_2$ ; if a *yellow* precipitate ( $\text{PbCrO}_4$ ) is produced,‡ a chromic compound is present in the substance under examination. Dissolve the residue in  $\text{HNO}_3$ , add  $\text{NaHO}$  in excess, warm the solution and filter, to the filtrate add  $\text{HNO}_3$  in excess, then  $\text{NH}_4\text{HO}$  in excess, and again warm the solution; if no precipitate should appear, even after some time (half an hour), no ALUMINIC COMPOUND is present.

158. *2d Method.*—The *group precipitate* after being carefully washed and dried is dissolved in strong  $\text{HNO}_3$ , and boiled, fragments of  $\text{KClO}_3$  being added from time to time till the oxidation is complete, which generally happens in four or five minutes if no water is present, as  $\text{H}_2\text{O}$  retards the oxidation;  $\text{KHO}$  is then added in excess,  $\text{Fe}_2\text{H}_6\text{O}_6$  and  $\text{Mn}_2\text{H}_6\text{O}_6$  will be precipitated if present; filter if necessary and add to the filtrate  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{HO}$ , which will precipitate  $\text{Al}_2\text{H}_6\text{O}_6$  if present; filter if necessary and add to the filtrate  $\text{BaCl}_2$  or  $\text{Ba}(\text{NO}_3)_2$ , a yellow precipitate of  $\text{BaCrO}_4$  will be produced if chromic oxide were present.—(Barth.)

\* See Fusion, in Part III.

† About one part of the precipitate to two of  $\text{Na}_2\text{CO}_3$  and two of  $\text{KNO}_3$ .

‡ The sodic carbonate and nitrate employed in the fusion must be entirely free from sulphate, otherwise, on the addition of  $\text{Pb}(\bar{\text{A}})_2$ , a white precipitate of  $\text{PbSO}_4$  will be formed, which the student might mistake for  $\text{PbCrO}_4$ .

TABLE IV.

BEHAVIOR OF THE FOURTH GROUP WITH THE SPECIAL REAGENTS.

$\text{Al}_2\text{O}_3$ .	$\text{Cr}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{FeO}$ .
L 1. $\text{Al}_2\text{O}_3$ and $\text{Al}_2\text{H}_6\text{O}_6$ are <i>white</i> .	M 1. $\text{Cr}_2\text{O}_3$ is green, and $\text{Cr}_2\text{H}_6\text{O}_6$ a <i>bluish-green powder</i> .	N 1. $\text{Fe}_2\text{O}_3$ and $\text{Fe}_2\text{H}_6\text{O}_6$ are of a <i>reddish-brown color</i> .	O 1. $\text{FeO}$ is <i>black</i> ; $\text{FeH}_2\text{O}_2$ is <i>white</i> .*
L 2. $\text{NH}_4\text{HO}$ , even in the presence of its salts, precipitates from <i>aluminic</i> solutions $\text{Al}_2\text{H}_6\text{O}_6$ , which an excess of the reagent <i>does not redissolve</i> .	M 2. $\text{NH}_4\text{HO}$ , even in the presence of its salts, precipitates from <i>chromic</i> solutions $\text{Cr}_2\text{H}_6\text{O}_6$ , which an excess of the reagent <i>does not redissolve</i> .	N 2. $\text{NH}_4\text{HO}$ , even in the presence of its salts, precipitates from <i>ferric</i> solutions $\text{Fe}_2\text{H}_6\text{O}_6$ , which an excess of the reagent <i>does not redissolve</i> .	O 2. $\text{NH}_4\text{HO}$ , <i>but not</i> in the presence of its salts, precipitates from <i>ferrous</i> solutions $\text{FeH}_2\text{O}_2$ , which an excess of the reagent <i>does not redissolve</i> .
L 3. The <i>fixed Alkalies</i> precipitate from <i>aluminic</i> solutions $\text{Al}_2\text{H}_6\text{O}_6$ , which is <i>soluble</i> in an excess of reagent, from which solution it may be again precipitated on the addition of $\text{NH}_4\text{Cl}$ .	M 3. The <i>fixed Alkalies</i> precipitate from <i>chromic</i> solutions $\text{Cr}_2\text{H}_6\text{O}_6$ , which is <i>soluble</i> in an excess of the reagent in the <i>cold</i> ; but on <i>boiling</i> the solution it is again precipitated.	N 3. The <i>fixed Alkalies</i> precipitate from <i>ferric</i> solutions $\text{Fe}_2\text{H}_6\text{O}_6$ , which is <i>insoluble</i> in an excess of the reagent.	O 3. The <i>fixed Alkalies</i> precipitate from <i>ferrous</i> solutions $\text{FeH}_2\text{O}_2$ , which is <i>insoluble</i> in an excess of the reagent.
L 4. $(\text{NH}_4)_2\text{CO}_3$ precipitates from <i>aluminic</i> solutions $\text{Al}_2\text{H}_6\text{O}_6$ . This precipitation is attended with an evolution of $\text{CO}_2$ .	M 4. $(\text{NH}_4)_2\text{CO}_3$ precipitates from <i>chromic</i> solutions $\text{Cr}_2\text{H}_6\text{O}_6$ , $\text{CO}_2$ being given off.	N 4. $(\text{NH}_4)_2\text{CO}_3$ precipitates from <i>ferric</i> solutions $\text{Fe}_2\text{H}_6\text{O}_6$ , $\text{CO}_2$ being given off.	O 4. $(\text{NH}_4)_2\text{CO}_3$ precipitates from <i>ferrous</i> solutions $\text{FeH}_2\text{O}_2$ , soluble in $\text{NH}_4\text{Cl}$ .

\* The student will most probably not obtain the precipitate of the colors here stated, as ferrous salts are rarely ever free from ferric salts, and the colors of the precipitate by this mixture are altered.

The fixed alkaline carbonates throw down from their solutions all the members of this group, some as oxides, the rest as carbonates. An excess of the reagent does not redissolve the precipitate.

The alkalies fail to precipitate the members of this group in the presence of non-volatile organic matter, such as starch, sugar, tartaric acid, etc.

159. *3d Method.*—Dissolve the precipitate in as small a quantity of boiling dilute HCl as possible; add to this acid solution when cold, a cold solution of NaHO or KHO, which will precipitate  $\text{Fe}_2\text{H}_6\text{O}_8$  (N3) *if Fe is present*;\* filter when a precipitate is produced and boil the *filtrate*, or the *solution* in which there was no precipitate, in a dish for a considerable time; if a precipitate is produced by the boiling, it is due to  $\text{Cr}_2\text{O}_3$ ; filter, and add to the filtrate, or to the solution which has failed to give a precipitate, HCl, until the solution is acid, then add *one grain* of  $\text{KClO}_4$ , and warm the solution so as to destroy all organic matter; add, lastly,  $\text{NH}_4\text{HO}$  in excess, and again warm the solution; if no precipitate should appear, allow it to stand for a short time (half an hour); if no precipitate should even then appear,  $\text{Al}_2\text{O}_3$  *is absent*.

PROPERTIES OF THE METALS, THE OXIDES, THE SULPHIDES, THE CHLORIDES, THE NITRATES, AND THE SULPHATES OF THE GROUP.

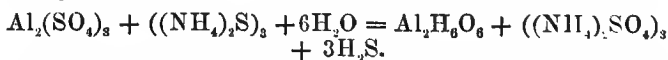
160. *The Metals.*—Cr and Al are not oxidized when heated even to redness in the open air. Fe oxidizes at the common temperatures in moist air. Al and Fe oxidize, Al only slowly, in an atmosphere of steam at a red heat,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  being formed. Fe decomposes also at a red heat  $\text{CO}_2$  and CO. Cr is not acted upon by any acid except HF.† Al is not acted upon in the cold by strong or dilute  $\text{HNO}_3$ , and very slowly at the boiling heat; dilute  $\text{H}_2\text{SO}_4$  dissolves it with difficulty, but HCl, either dilute or concentrated, dissolves it readily even at low temperatures,  $\text{Al}_2\text{Cl}_6$  being formed. Pure Fe is scarcely acted upon by acids at the ordinary temperature, but dissolves

\* Manganese, if present, will also be precipitated by the sodic or potassic solution, so that a precipitate may be produced by the alkali when ferric oxide is absent.

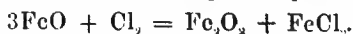
† The properties of Cr differ considerably according to the manner in which it is prepared, the difference depending doubtless on the state of aggregation. Cr made by Peligot's process oxidizes with great facility, taking fire in the air even at a heat below redness; it also dissolves in dilute  $\text{H}_2\text{SO}_4$  and HCl, and is oxidized by  $\text{HNO}_3$ . The properties of most metals vary very much with the state of aggregation; thus, even lead and several other metals, which will only combine with the oxygen of the air with vivid combustion at very high temperatures when in masses, will when in a state of fine powder combine with the oxygen of the air with vivid combustion at the ordinary temperature of the atmosphere.

with the aid of heat, H being evolved; but Fe as usually obtained dissolves readily in dilute mineral acids, but strong  $\text{HNO}_3$  covers it with a film of  $\text{Fe}_2\text{O}_3$ , which prevents the further action of the acid, whether dilute or undilute; but reducing agents remove the film, the *passive* iron is thereby again rendered active and capable of dissolving in dilute  $\text{HNO}_3$ . Al is not acted on by  $\text{H}_2\text{S}$  or by  $(\text{NH}_4)_2\text{S}$ ;  $\text{KHO}$  or  $\text{NaHO}$  in a state of fusion do not act upon it, but their solutions dissolve it readily, forming  $\text{Al}_2\text{Na}_3\text{O}_8$  or  $\text{Al}_2\text{K}_3\text{O}_8$  and H being evolved. Cr and Fe are oxidized by fusion with  $\text{KNO}_3$ ,  $\text{K}_2\text{CrO}_4$ , and  $\text{K}_2\text{FeO}_4$  being formed. Al may be obtained by passing  $\text{Al}_2\text{Cl}_6$  in vapor over Na, and Cr may be obtained by passing the vapor of  $\text{Cr}_2\text{Cl}_6$  over Zn.

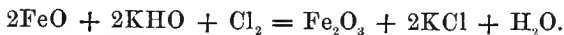
161. *The Oxides.*— $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$  may be obtained by igniting their hydrates;  $\text{FeO}$  by precipitating  $\text{FeH}_2\text{O}_2$  from a ferrous salt by an alkali, and boiling it in a vessel from which O is excluded, the hydrate being rendered anhydrous below the boiling point. They are not altered by heat except  $\text{Fe}_2\text{O}_3$ , which at a white heat is converted into  $\text{Fe}_3\text{O}_4$ , and  $\text{FeO}$  is converted, on exposure to air without the aid of heat, into  $\text{Fe}_2\text{O}_3$ .  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  are not reduced by H,  $\text{Al}_2\text{O}_3$  is not reduced by C, and  $\text{Cr}_2\text{O}_3$  is reduced by C at a white heat, but only at the points of contact; the oxides of Fe are reduced by H and C with the aid of heat.  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  are unaltered on being heated with S, but  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$  are converted by it into  $\text{FeS}$  with evolution of  $\text{SO}_2$ .  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  are not converted into chlorides by Cl unless they are mixed with C (see note, page 52); Cl displaces the O in the iron oxides.  $\text{FeO}$  and  $\text{Cr}_2\text{O}_3$  are, with one other oxide (the molybdic), the only oxides which melt at a temperature below that of the metal from which they are produced. *The hydrates* may be obtained by adding to a solution of their salts  $\text{NH}_4\text{HO}$ , or one of the fixed alkalies, or in the case of  $\text{Al}_2\text{H}_6\text{O}_6$ ,  $\text{Cr}_2\text{H}_6\text{O}_6$ , and  $\text{Fe}_2\text{H}_6\text{O}_6$  by adding  $(\text{NH}_4)_2\text{CO}_3$ , as shown in Table IV.  $\text{Al}_2\text{H}_6\text{O}_6$  and  $\text{Cr}_2\text{H}_6\text{O}_6$  may also be obtained by adding  $(\text{NH}_4)_2\text{S}$  to a solution of their salts with evolution of  $\text{H}_2\text{S}$ , thus:—



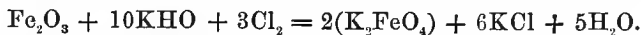
$\text{FeO}$  is the only member which is acted upon by Cl when suspended in pure  $\text{H}_2\text{O}$ , or in a solution moderately alkaline. The following is the change in  $\text{H}_2\text{O}$ :—



If it be suspended in an alkaline liquid the following is the reaction :—

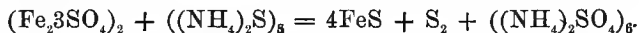


$\text{Fe}_2\text{O}_3$  may be converted into a higher oxide (ferric acid) by  $\text{Cl}$  if the solution contains a large quantity of  $\text{KHO}$ , thus :



These oxides and their hydrates are insoluble in  $\text{H}_2\text{O}$ , but they dissolve in the dilute mineral acids; after ignition, however, they dissolve with great difficulty, even in the concentrated mineral acids; but even after ignition, if fused with  $\text{KHSO}_4$ , they dissolve readily along with the other fused particles in  $\text{H}_2\text{O}$ . Although it has just been stated that these oxides and their hydrates are insoluble in  $\text{H}_2\text{O}$ , a modification of aluminic hydrate, which will be noticed under the remarks on Aluminic Compounds (par. 167), is soluble in  $\text{H}_2\text{O}$ , and it appears probable there is also a soluble ferric hydrate.

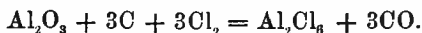
162. *The Sulphides*.—It has already been stated that aluminic and chromic sulphides are not formed in the humid way, but they may be obtained by passing the vapors of  $\text{CS}_2$  over the  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  intensely heated. These sulphides are black, they are decomposed by  $\text{H}_2\text{O}$  into hydric oxides,  $\text{H}_2\text{S}$  being evolved.  $\text{Fe}_2\text{S}_3$  and  $\text{FeS}$  may be obtained in the anhydrous state by the direct combination of  $\text{Fe}$  and  $\text{S}$ ; the color of the first is yellowish-gray and the other yellow.  $\text{Fe}_2\text{S}_3$  may be obtained in the hydrated state by dropping a solution of a ferric salt into a solution of an alkaline sulphide which is in excess, or by passing  $\text{H}_2\text{S}$  over the dry hydrate; this sulphide is speedily altered by exposure to air,  $\text{Fe}_2\text{O}_3$  being formed and  $\text{S}$  set free;\* if the alkaline sulphide is added to the solution of the ferric salt, ferrous sulphide is formed and  $\text{S}$  set free; thus :—



\* Ferric hydrate is employed to some extent in removing  $\text{H}_2\text{S}$  from coal-gas; for this purpose it is mixed with sawdust and placed in layers about twelve inches deep on perforated shelves; when the mixture ceases to remove the  $\text{H}_2\text{S}$ , ferric oxide is reproduced and  $\text{S}$  set free by exposing the  $\text{Fe}_2\text{S}_3$  to a current of air; the revived oxide is again employed, and this continues until the accumulation of  $\text{S}$  in the mixture impairs its absorbing power; the  $\text{S}$  is then utilized by the sulphuric acid manufacturer, and the  $\text{Fe}_2\text{O}_3$  which remains may be again employed for purifying the gas.

Alkaline sulphides precipitate from solutions of ferrous salts FeS in the hydrated state; its color is black; it is insoluble in alkalis and alkaline sulphides, but dissolves readily in HCl and HNO<sub>3</sub>; it oxidizes quickly on exposure to air, turning reddish-brown, Fe<sub>2</sub>O<sub>3</sub> being formed and S set free.

163. *The Chlorides.*—Al<sub>2</sub>Cl<sub>6</sub>, Cr<sub>2</sub>Cl<sub>6</sub>, and Fe<sub>2</sub>Cl<sub>6</sub> may be obtained in the hydrated state by dissolving the anhydrous chlorides in water or the sesquioxides of these metals in HCl; these hydrous chlorides cannot be rendered anhydrous by heating them in the air, as they are decomposed into the corresponding metallic oxides, HCl being evolved. Al<sub>2</sub>Cl<sub>6</sub>, Cr<sub>2</sub>Cl<sub>6</sub>, and Fe<sub>2</sub>Cl<sub>6</sub> may be obtained in the anhydrous state; the first two by heating a mixture of Al<sub>2</sub>O<sub>3</sub> or Cr<sub>2</sub>O<sub>3</sub> with C and igniting in a current of dry Cl; the following is the reaction:—



Fe<sub>2</sub>Cl<sub>6</sub> may be obtained by passing dry Cl over Fe heated to redness; these anhydrous chlorides are volatile, deliquescent, and dissolve readily in H<sub>2</sub>O with considerable evolution of heat; Fe<sub>2</sub>Cl<sub>6</sub> is reduced by H<sub>2</sub>S and other reducing agents to the state of ferrous chloride. Anhydrous FeCl<sub>2</sub> may be prepared by passing dry HCl gas over ignited Fe; it may be obtained in the hydrated state by dissolving Fe in HCl; it is very soluble in H<sub>2</sub>O, and if heated in the open air Cl escapes and Fe<sub>2</sub>O<sub>3</sub> remains; it is converted into Fe<sub>2</sub>Cl<sub>6</sub> on passing Cl into its solution. Al<sub>2</sub>Cl<sub>6</sub> is not decomposed at any temperature by H; if H be passed over perfectly anhydrous Cr<sub>2</sub>Cl<sub>6</sub>, very gently heated, CrCl<sub>2</sub> is formed; if the heat be strong, Cr is separated; the iron chlorides are decomposed by H with the aid of heat, HCl being formed and Fe remaining.

164. *The nitrates* may be obtained by dissolving the oxides in HNO<sub>3</sub>; they are soluble in H<sub>2</sub>O, and readily decomposed by heat.

165. *The sulphates*, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> may be obtained by dissolving the hydrates of these metals in H<sub>2</sub>SO<sub>4</sub>; the first is also formed by adding to clay which has been gently heated H<sub>2</sub>SO<sub>4</sub> and then heating the mixture for a considerable time; the latter may be prepared by adding to every 1 eq. of FeSO<sub>4</sub> in solution  $\frac{1}{2}$  eq. of H<sub>2</sub>SO<sub>4</sub>, and then adding to the heated liquid HNO<sub>3</sub> in small quantities as long as any red fumes are given off. These sulphates are soluble in H<sub>2</sub>O; they are decomposed by heat, the

metallic oxides being left; they and  $Mn'''_2(SO_4)_3$  form with the alkaline sulphates double salts, which are termed alums. The general formula for this class of salts is  $M'''_2(SO_4)_3, M_2SO_4 + 24H_2O$ . A solution of  $Fe_2(SO_4)_3$ , especially if it contains a little free acid, dissolves many metals, even Ag, and the  $Fe_2(SO_4)_3$  is reduced to  $FeSO_4$ .  $FeSO_4$  may be obtained by dissolving Fe in  $H_2SO_4$ ; it is also formed by the conversion of iron pyrites ( $FeS_2$ ) into FeS, and this by oxidation into  $FeSO_4$ . It crystallizes with seven atoms of  $H_2O$ ; the crystals, when pure, are bluish-green, but if they contain ferric sulphate they are grass green; at a red heat  $FeSO_4$  is decomposed into  $Fe_2O_3$ ,  $SO_2$ , and  $SO_3$ ; the little water which distils over forms with the  $SO_3$  the Nordhausen sulphuric acid.\*

166. *The general characters of the salts of this group.*—Aluminic salts, with the exception of the chloride, are colorless, both in the hydrous and anhydrous states. Chromic oxide forms at least two varieties of salts; there is a variety which is uncrystallizable and of a *green* color, another variety is crystallizable and of a *violet* color; the solutions of the violet salts change to green on heating, and the green solutions generally transmit a red light. Ferric salts are nearly *white* in the anhydrous, and *yellow* or *yellowish-red* in the hydrous, state; the color of the solutions is *brownish-yellow*. Ferrous salts are *white* in the anhydrous and *bluish-green* in the hydrous state; their solutions, if concentrated, have a *greenish* color. Ferric salts are converted into ferrous ones by reducing agents, as nascent H,  $H_2S$ ,  $SO_2$ , Fe, Zn,  $SnCl_2$ , etc. Ferrous salts are converted into ferric ones by oxidizing agents, as O, Cl,  $HNO_3$ , etc. Solutions of the ferrous salts rapidly absorb O from the air, and if the solution is neutral a yellow basic ferric salt is deposited. The soluble neutral salts of the metals of this group *red*den litmus paper, and are decomposed by heat. The members of this group are precipitated by  $(NH_4)_2S$ , Al and Cr, as hydric oxides; consequently  $H_2S$  is always evolved when  $(NH_4)_2S$  is added to a solution containing either or both these metals. FeS is always formed when  $(NH_4)_2S$  is added either to a solution of ferrous or ferric salts.  $Fe_2O_3$ , and also  $Al_2O_3$ , are frequently sepa-

\* This acid has a composition corresponding to  $H_2SO_4$ ,  $SO_3$ ; it is principally prepared at the town of Nordhausen, in Saxony, by drying crystallized ferrous sulphate at a moderate heat to expel the water of crystallization, and then distilling the dried sulphate in earthen retorts.

rated from their solutions, and from other bases, by adding an alkaline acetate or formiate, previously adding to the solution one of  $\text{Na}_2\text{CO}_3$  or  $(\text{NH}_4)_2\text{CO}_3$  until the precipitate which is formed *only just* redissolves on stirring; the formiate or acetate is then added, and the solution boiled; ferric and aluminic acetates or formiates are formed in the first instance, and are decomposed by boiling into *insoluble* basic acetates or formiates.  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  are completely precipitated from solutions of their salts *in the cold* by digesting in the solutions finely powdered  $\text{BaCO}_3$  or  $\text{CaCO}_3$ ; they are precipitated principally in the state of hydrates and partly as basic salts. Other insoluble carbonates also precipitate them; thus, if it is desired to purify  $\text{MnCl}_2$  or  $\text{ZnSO}_4$  from a ferric salt, it may be accomplished by boiling the solution of the  $\text{MnCl}_2$  with  $\text{MnCO}_3$ , and the solution of the  $\text{ZnSO}_4$  with  $\text{ZnCO}_3$ .  $\text{Cr}_2\text{O}_3$  is also precipitated from its solutions by digesting with  $\text{BaCO}_3$ , but the precipitation takes place *in the cold* only after long-continued digesting.  $\text{BaCO}_3$  does not precipitate  $\text{FeO}$  from solutions of ferrous salts, with the exception of the sulphate, when it is digested in the solutions in the cold. The members of this group, with the exception of  $\text{FeO}$ , differ from the preceding group by being insoluble in  $\text{NH}_4\text{HO}$ , and they and the third group differ from those of the fifth and sixth by not being precipitated by  $\text{H}_2\text{S}$  in the presence of *free* mineral acids.

REMARKS ON INDIVIDUAL MEMBERS OF THIS GROUP, WITH  
ADDITIONAL SPECIAL TESTS.

167. *Al and its compounds.*—Al is a bluish-white metal, very malleable, ductile and sonorous; it is very light, its sp. gr. being about 2.5; its sp. heat is very great, its melting-point is intermediate between the melting-points of Zn and Ag, but nearer to the former; it is a better conductor of heat than Ag, and about equal to it as a conductor of electricity. The now well-known alloy of aluminum and copper, viz. *aluminum bronze*, contains 10 per cent. of Al. In combination it is very abundant in nature; it forms not only the basis of common clay, but is likewise a principal ingredient in many of the precious stones. As  $\text{Al}_2\text{O}_3$ , with slight traces of  $\text{SiO}_2$  and  $\text{Fe}_2\text{O}_3$ , it forms the CORUNDUM, SAPPHIRE, RUBY, DIAMANT SPAR, etc. As hydrate, it is known under the names DIASPORE and GIBBSITE. Combined with silica and glucina, it forms the EMERALD, BERYL, EUCLASE, and CHRYSOBERYL.  $\text{Al}_2\text{O}_3$  has the property of



combining very intimately with certain kinds of organic matter, especially coloring matters; it attaches itself to the fibres of cloth, and retains in the cloth the power of attracting and retaining coloring matters; its salts are therefore extensively employed as mordants. It is obtained in a form soluble in  $H_2O$  by exposing a dilute solution of an aluminic acetate to a temperature of  $100^\circ C.$  in a close vessel for several days; this solution is coagulated by mineral and most vegetable acids, by alkalies and decoctions of dye woods, but the alumina in this form does not act as a mordant.  $Al_2O_3$  is the only oxide known of  $Al$ ; it is regarded as a sesquioxide on account of its isomorphism with, and general resemblance in properties to,  $Fe_2O_3$ .

168. If aluminic compounds be ignited upon charcoal by the blowpipe flame, afterwards moistened with a few drops of  $Co(NO_3)_2$ , and again strongly heated, the mass assumes a BLUE COLOR on cooling. This can only be used as a confirmatory test, as other substances, phosphates and readily fusible salts, exhibit the same reaction.

*Characteristic.*—The reactions with  $NH_4HO$ ,  $KHO$ , and the blowpipe test.

169. *Cr and its compounds.*—The principal mineral of  $Cr$ , and from which the oxide is obtained, is the CHROME IRON ( $FeO, Cr_2A_3$ ), which is found principally in Sweden, in the Uralian Mountains, and in America; it is scarcely attacked by any of the acids.

170. On fusing any chromic compound with  $KNO_3$  or  $NaNO_3$ , yellow *chromate* of the alkali ( $M_2CrO_4$ ) is formed, which is soluble in water, and by adding to the solution acetic acid in excess, and then  $Pb\bar{A}_2$ , yellow  $PbCrO_4$  precipitates; this test distinguishes it from all other substances. In the fixed alkalies, a small quantity of  $Cr_2O_3$  in the presence of a large quantity of  $Fe_2O_3$  is totally insoluble; but a small quantity of the latter dissolves readily when a large quantity of the former is present. Under these circumstances the two oxides are best separated from each other by fusing the mixed substances with  $KNO_3$  and  $Na_2CO_3$ . On treating the fused mass with water, the  $K_2CrO_4$  dissolves, but the  $Fe_2O_3$  does not. The solution may be tested with  $Pb\bar{A}_2$ .

171. If a solution of  $Cr_2O_3$  in  $NaHO$  or  $KHO$  is boiled with  $PbO_2$  in excess for a short time, the  $Cr_2O_3$  reduces some of the  $PbO_2$ ,  $PbCrO_4$  being formed, which dissolves

in the alkaline solution; if to the filtered liquid acetic acid be added in excess, the  $\text{PbCrO}_4$  precipitates.

172. *Borax* dissolves chromic compounds, both in the inner and outer blowpipe flame; the bead, on cooling, assumes an EMERALD GREEN COLOR. *Microcosmic salt* has the same effect.

*Characteristic.*—The color of its salts, its conversion by oxidizing agents into chromic acid, and the blowpipe test.

173. Three other oxides of Cr are known, viz.,  $\text{CrO}$ , a base;  $\text{CrO}$ ,  $\text{Cr}_2\text{O}_3$ , corresponding to magnetic oxide of iron; and  $\text{CrO}_3$ , an anhydride, which forms salts with bases, and is noticed amongst the acids.  $\text{CrO}$  is known only in the hydrated state; it is obtained by adding  $\text{KHO}$  to a solution of  $\text{CrCl}_2$ ; it absorbs  $\text{O}$  with great rapidity; it decomposes even  $\text{H}_2\text{O}$ ,  $\text{H}$  being evolved, and the other oxide ( $\text{CrO}$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{H}_2\text{O}$ ) in the hydrated state being formed. Chromic oxide and many of the chromates are employed as coloring materials in painting on porcelain and in calico printing.

174. *Fe and its compounds.*—Very little is known about perfectly pure  $\text{Fe}$ ; it is met with in the arts in three different forms, *cast iron*, *malleable iron*, and *steel*; each of these varieties contains carbon and other foreign matters, but the differences of character in these varieties appear to be chiefly due to the different proportions of  $\text{C}$  which are disseminated through, or combined with, the metal. The ores of iron are numerous, the most valuable are *specular iron ore*, red *hæmatite*, varieties of  $\text{Fe}_2\text{O}_3$ , brown *hæmatite* ( $2\text{Fe}_2\text{O}_3$ ,  $3\text{H}_2\text{O}$ ), *spathic iron* or *carbonate of iron* ( $\text{FeCO}_3$ ), *clay ironstone* and the *black band* are an impure ferrous carbonate, and the *magnetic iron ore*, or *loadstone* ( $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$ ).

175. *Potassic ferrocyanide* ( $\text{K}_4\text{FeCy}_6$ ) produces in *ferrous* solutions a white precipitate of  $\text{FeK}_2\text{FeCy}_6$ , which speedily becomes *blue* by absorbing oxygen from the air. Free alkalies prevent its formation, and they readily decompose it. It is insoluble in the dilute acids.

176.  $\text{K}_4\text{FeCy}_6$  produces, even in highly dilute *ferric* solutions, a beautiful blue precipitate of Prussian blue,  $\text{Fe}_4(\text{FeCy}_6)_3$ , which is insoluble in acids, but is decomposed by the alkalies; in highly dilute solutions only a blue tinge is produced at first; after long standing a scanty precipitate is formed. The same precautions are required in this case as in par. 177.

177. *Potassic ferricyanide* ( $\text{K}_3\text{Fe}_2\text{Cy}_{12}$ ) produces in *fer-*

rous solutions a beautiful blue-colored precipitate of TURNBULL'S BLUE ( $\text{Fe}_3\text{Fe}_2\text{Cy}_{12}$ ), which is insoluble in  $\text{HCl}$ , but is decomposed by the alkalies. In highly dilute solutions only a bluish-green coloration is produced. If the solution is alkaline, it must be acidified with acetic acid; if it is acid, and the acidity is caused by one of the mineral acids, as they decompose both the potassic ferri- and ferro-cyanides, rendering their solutions green, an alkaline acetate must be added in sufficient quantity so that the base of the acetate may neutralize the free mineral acid.

178.  $\text{K}_6\text{Fe}_2\text{Cy}_{12}$  deepens the color of the solution of ferric salts to a ruddy brown, but causes no precipitate; if the ferricyanide contains a trace of ferrocyanide,\* it will impart to the ferric solution a greenish tinge.

179. Potassic sulphocyanide ( $\text{KCyS}$ ) produces in neutral and even in moderately acid ferric solutions a very intense blood red, arising from the formation of  $\text{Fe}_2(\text{CyS})_3$ , which is soluble. The color disappears on the addition of an alkaline acetate, but is restored by adding to the solution dilute  $\text{HCl}$ ; it also disappears on the addition of alkalies, or of a large quantity of strong acid. This is by far the most delicate test for ferric compounds.

180. *Flame reactions.*—*Reduction on charcoal splinter* gives no metallic bead or ductile lustrous particles; the finely divided metal forms a black brush on the end of the magnetized knife-blade; this, when rubbed off on paper and dissolved in a drop of aqua regia, yields a yellow spot when warmed over the flame, which, when moistened with  $\text{K}_4\text{FeCy}_6$ , gives a deep coloration of *Prussian blue*. The yellow spot moistened with  $\text{NaHO}$ , and then held for a few moments in a vessel with bromine vapor, gives, on a second addition of soda, no coloration of a higher oxide.

181. *Borax bead.*—"In the oxidizing flame, when hot, yellow to brownish-red; when cold, yellow to brownish-yellow; reducing flame, bottle-green."—*Bunsen*.

*Characteristic.*—For ferrous compounds, the reactions with  $\text{K}_6\text{Fe}_2\text{Cy}_{12}$ ; for ferric compounds, the reactions with  $\text{K}_4\text{FeCy}_6$  and  $\text{KCyS}$ .

182. Two other iron oxides are known, viz., the black or magnetic oxide,  $\text{Fe}_3\text{O}_4$ , which may be viewed as a compound of  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$ , and ferric acid. The magnetic oxide

\* The solution of potassio ferricyanide ought to be made as it is wanted, as it decomposes when in a state of solution, a trace of ferrocyanide being formed.

occurs in nature; it may be formed, as we have already noticed, by passing steam over Fe, and it may be obtained in the hydrated state by dissolving a ferrous and ferric salt in equal atomic proportions, and adding to the solution KHO or NaHO. Ferric acid,  $H_2FeO_4$ , may be obtained, we have seen, by fusing Fe with  $KNO_3$  (160), or by passing Cl into an alkaline solution of  $Fe_2O_3$  (161).

Answers to the following exercises must be written out.

## EXERCISES.

64. Name the substances which will be precipitated when  $(NH_4)_2S$  is added to an aqueous solution containing  $Al_2(SO_4)_3$ ,  $Cr_2Cl_6$ ,  $Fe_2Cl_6$ ,  $FeSO_4$ ,  $ZnSO_4$ ,  $Co(NO_3)_2$ , and  $K_2SO_4$ , and the form in which they will be precipitated.

65. A solution which has to be examined for the members of this and the preceding groups is alkaline to test-paper; the alkalinity is found to be due to the presence of  $Na_2CO_3$ ; what members must be absent?

66. I have a quantity of zincic sulphate which contains some ferrous sulphate; how must I get rid of the iron so that after its removal no other salt but the zinc sulphate will remain in solution?

67. How are ferrous and ferric oxides distinguished from each other? Illustrate your answer by equations.

68. The members of the third and fourth groups have been precipitated together by  $(NH_4)_2S$ ; how must the precipitate be treated so as to isolate and detect each of the members (the phosphates and oxalates not being present)?

69. How are potassic ferrocyanide and ferricyanide prepared?

70. I require some ferric chloride, and I have only some ferrous sulphate; how must I proceed so as to obtain from the latter salt the  $Fe_2Cl_6$ ?

71. How can the precipitation of  $Fe_2H_6O_6$ ,  $Al_2H_6O_6$ , and of  $Cr_2H_6O_6$ , from solutions of their salts by the alkalies, be prevented?

72. Ferric oxide is employed to purify coal gas; on ceasing to purify it, it is exposed to the air; the exposure restores its purifying powers. State what impurities it removes, and how the air revivifies it; state what impurity calcic hydrate removes which the iron oxide does not remove.

73. You are given a solution which is neutral to test-paper, and which can contain only the members of this

and the preceding groups: what members must be absent, and what salts of those members *which may be present* must be absent either from their insolubility or from their being alkaline or acid to test-paper? (The student is only expected to answer it to the extent of the salts with which he has been made acquainted in the first four groups.)

74. I fuse in a furnace 2 parts of chrome iron mixed with 1 part of potassic nitrate; I treat the fused mass with water, and add  $\text{H}_2\text{SO}_4$  or  $\text{HNO}_3$  until the solution is acid to test-paper; I then evaporate the solution to the crystallizing point, and allow time for the crystallization. State what substances are formed in the fusion, what substances are dissolved and what are not dissolved by the water, what alteration the added acid effects, and what substance crystallizes out.

75. There is present in a solution  $\text{Fe}_2\text{Cl}_6$ ,  $\text{Al}_2\text{Cl}_6$ ,  $\text{CoCl}_2$ ,  $\text{MnCl}_2$  and  $\text{NiCl}_2$ ; the solution is placed in a flask,  $\text{BaCO}_3$  is added a little in excess, the flask is corked and allowed to stand some time in the cold, with occasional shaking. What occurs? The mixture is filtered into a flask, the filtrate is slightly acidulated with  $\text{HCl}$ ,  $\text{Cl}$  is then transmitted through it to saturation,  $\text{BaCO}_3$  or  $\text{CaCO}_3$  is then added slightly in excess, the mixture is allowed to stand some hours in the cold and shaking it repeatedly. State the changes which ensue.

76. How is ammoniac sulpho-cyanide prepared?

77. I wish to prepare some pure  $\text{MnCl}_2$  from the waste product obtained in the manufacture of  $\text{Cl}$  by acting on  $\text{MnO}_2$  with  $\text{HCl}$ ; it contains, in addition to the  $\text{MnCl}_2$ ,  $\text{Fe}_2\text{Cl}_3$  and  $\text{HCl}$ . How shall I proceed? I have another quantity of the waste product, containing in addition to the impurities already named some  $\text{CuCl}_2$ ,  $\text{CoCl}_2$ , and  $\text{NiCl}_2$ ; how shall I proceed in this case to obtain pure  $\text{MnCl}_2$ ? Describe a different method in each case.

78. A colorless solution is given you to examine for the members of this and the preceding groups; what members are probably absent?

79. Enumerate the chief ores of iron, and give their composition.

80. There is present in an acetic acid solution  $\text{Al}'''$ ,  $\text{Fe}'''$ ,  $\text{Co}''$ ,  $\text{Zn}''$ ,  $\text{Ni}''$ , and  $\text{Mn}''$ ;  $\text{H}_2\text{S}$  is passed through it; what changes, if any, take place?

81. You have to examine a mixture which can only contain ferrous, ferric, calcic, magnesic, potassic, and ammoniac

salts: describe the methods you would adopt in the examination.

82. Describe the manufacture of aluminum.

83. Give the composition of Nordhausen sulphuric acid, and state how it is prepared.

84. How would you prepare anhydrous  $\text{Fe}_2\text{Cl}_6$  and anhydrous  $\text{Al}_2\text{Cl}_6$ ?

85. How would you prepare  $\text{Fe}_2\text{S}_3$ ?

86. Describe a method for the preparation of  $\text{PbO}_2$ .

*The following SALTS, being insoluble in Neutral and Alkaline Solutions, are precipitated along with the members of the Fourth Group.\**

ALUMINIC, CHROMIC, AND FERRIC PHOSPHATES; THE PHOSPHATES OF THE ALKALINE EARTHS; BARIC, STRONTIC, AND CALCIC OXALATES.

183. Aluminic phosphate varies considerably in composition, according to the proportions of the acting solutions and the temperature at which they are mixed; it behaves in the same way with reagents as  $\text{Al}_2\text{O}_3$ , with this exception, that it is insoluble in acetic acid, whilst  $\text{Al}_2\text{O}_3$  is soluble. The presence of  $\text{PO}_4$  when combined with  $\text{Al}_2\text{O}_3$ , may be detected by the following method: After having dissolved the aluminic compound in a small quantity of  $\text{HCl}$ ,  $\text{H}_2\text{T}$  must be added and then  $\text{NH}_4\text{HO}$  in excess. If on the addition of  $\text{MgSO}_4$  to this solution a precipitate be formed,  $\text{PO}_4$  is present. When the quantity of acid present is small, the precipitate will not appear until after the lapse of some time; in all cases the formation of the precipitate is much promoted by agitation.

184.  $\text{PO}_4$  in combination with  $\text{Al}_2\text{O}_3$  may also be detected in the following way: "Add  $\text{Na}_2\text{CO}_3$  to the  $\text{HCl}$  solution until the free acid is nearly neutralized; mix with  $\text{BaCO}_3$  in excess, add solution of  $\text{NaHO}$  or  $\text{KHO}$ , and boil. This process gives the  $\text{Al}_2\text{O}_3$  in solution, the  $\text{PO}_4$  in a precipitate of baric phosphate. Dissolve this precipitate in  $\text{HCl}$ , decompose by  $\text{H}_2\text{SO}_4$ , filter, and test the filtrate with  $\text{MgSO}_4$ , with addition of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{HO}$ ."—*Fresenius*.

185.  $\text{PO}_4$  may be detected in almost all salts and most

\* The student will do well to omit this section of the group until he has had some practice in detecting the more simple combinations of acid and base.

minerals containing it by the ammonic molybdate test (see par. 428).

186. CHROMIC PHOSPHATE behaves in the same way with reagents as  $\text{Cr}_2\text{O}_3$ , with this exception, that it is insoluble in acetic acid, in which reagent the latter is soluble. The presence of  $\text{PO}_4$  when combined with  $\text{Cr}_2\text{O}_3$  may be detected in the same way as when combined with alumina. To ascertain whether  $\text{Cr}_2\text{O}_3$  and the chromic phosphate are both present in the precipitate produced by boiling the fixed alkaline solution, dissolve the precipitate produced on boiling in  $\text{HCl}$ , add an *alkaline acetate* in excess; if a precipitate is produced, the PHOSPHATE is present, filter off, and to the filtrate add  $\text{NH}_4\text{HO}$  in excess; if a precipitate is produced, the OXIDE is present.

187. Ferric phosphate, like aluminic phosphate, varies considerably in composition, and from the same causes; it behaves in the same way with reagents as  $\text{Fe}_2\text{O}_3$ , with this exception, that it is insoluble in acetic acid, in which reagent the latter is soluble.  $(\text{NH}_4)_2\text{S}$  decomposes IRON PHOSPHATE,\* precipitating the metal in the state of sulphide whilst the acid remains in solution in combination with the ammonia. The acid is therefore sought for in the filtrate, and not in the precipitate, when  $(\text{NH}_4)_2\text{S}$  has been employed as the precipitating reagent. The same method may be employed for the detection of  $\text{PO}_4$ , when combined with  $\text{Fe}$ , as is employed when this acid is in combination with  $\text{Al}$ .

188. The different calcic ortho-phosphates are soluble in acetic acid. They may be decomposed in several ways. The following are those which are most applicable in qualitative analysis: 1. Dissolve the phosphate in a small quantity of  $\text{HCl}$ ; add to the solution an *alkaline acetate*, and after that a few drops of  $\text{Fe}_2\text{Cl}_3$  (consult par. 427). FERRIC PHOSPHATE will be precipitated, whilst the  $\text{Ca}$  will remain in solution along with the excess of the  $\text{Fe}_2\text{Cl}_3$ . To detect the  $\text{Ca}$ , precipitate  $\text{Fe}$  by  $(\text{NH}_4)_2\text{S}$ , and add to the filtrate  $\text{H}_2\text{O}$ . If a precipitate be produced,  $\text{Ca}$  is present. 2. Dissolve the phosphate in a small quantity of  $\text{HNO}_3$ ; add to this solution  $\text{HgNO}_3$ , and then  $\text{NH}_4\text{HO}$  slightly in excess; MERCUROUS PHOSPHATE along with the excess of  $\text{Hg}_2\text{O}$  will be precipitated, whilst the  $\text{Ca}$  will remain in solution, from which solution it will be thrown

\* Aluminic and chromic phosphates are not decomposed by  $(\text{NH}_4)_2\text{S}$ ; they are precipitated unchanged by that reagent.

down on the addition of  $H_2\bar{O}$ . Boil the mixed precipitate of mercurous phosphate and oxide in  $(NH_4)_2S$ ; filter, and to the filtrate add  $NH_4Cl$  and  $MgSO_4$ ; if a precipitate be produced, it proves the presence of  $PO_4$ . The above remarks upon CALCIC PHOSPHATES apply to the corresponding BARIC, STRONTIC, and MAGNESIC salts.

189. CALCIC OXALATE is insoluble in acetic acid. By ignition, this salt, like all the other oxalates, is decomposed, a carbonate being left. To separate the  $\bar{O}$  from the Ca, to its solution in  $HNO_3$  add  $HgNO_3$ ;  $Hg_2\bar{O}$  will be precipitated, whilst  $Ca(NO_3)_2$  will remain in solution along with the excess of  $HgNO_3$ . To detect Ca, remove the Hg from the solution by  $NH_4HO$ , and add to the filtrate  $H_2\bar{O}$ .  $Hg_2\bar{O}$  is decomposed by boiling it in  $(NH_4)_2S$ ,  $Hg_2S$  being precipitated, whilst the acid remains in combination with ammonia, in which solution it may be detected on the addition of any soluble calcic salt. The above remarks apply to the corresponding BARIC and STRONTIC salts.

190. *The following precautions are to be attended to in the analysis of this section:* Before dissolving the precipitate produced by  $NH_4HO$ , it must be completely freed by washing from all trace of that reagent. Frequently a small precipitate will appear after boiling the  $NaHO$  solution, when Cr is absent; the presence of this member must therefore in all cases be confirmed by other tests.  $Al_2O_3$  and its phosphates are sometimes overlooked by the operator, from his neglecting to add acetic acid in excess. The precipitate produced by  $NaHO$ , after being well washed, should be dissolved in as small a quantity of  $HNO_3$  as possible, to which solution a moderate quantity of  $H_2\bar{T}$  should be afterwards added, and finally  $NH_4HO$  in excess; the solution ought, after the addition of these reagents, to be well agitated, and time allowed for the separation of the precipitate. In testing for  $PO_4$  in the ammoniac solution, a precipitate will frequently be formed on the addition of  $MgSO_4$  when  $PO_4$  is absent. To distinguish the phosphate precipitate from this, the precipitate produced ought to be dissolved in  $H_2\bar{T}$ , and  $NH_4HO$  added in excess. If a precipitate again appears, after agitating the liquid and allowing it to stand, it must be due to the presence of  $PO_4$ . The precipitate produced by  $NH_4HO$  in the  $H_2\bar{T}$  solution must be well washed before dissolving it in dilute  $HNO_3$ . A slight turbidness will generally be formed on the addi-



TABLE V.—PRECIPITATE PRODUCED BY  $\text{NH}_4\text{HO}$  IN THE  $\text{H}_2\text{S}$  FILTRATE.  
*Dissolve in boiling dilute  $\text{HNO}_3$ .—Add an excess of  $\text{NaHO}$  in the cold.*

FILTRATE		PRECIPITATE	
CHROMIC OXIDE, CHROMIC PHOSPHATE, ALUMINIC OXIDE, ALUMINIC PHOSPHATE. <i>Boil for some time.</i>		FERRIC OXIDE, FERRIC PHOSPHATE, AND, WHEN IN COMBINATION WITH $\bar{\text{O}}$ OR $\text{PO}_4$ , Ba, Sr, Ca; ALSO Mg WHEN IN COMBINATION WITH $\text{PO}_4$ . <i>Dissolve in boiling dilute <math>\text{HNO}_3</math>, then add <math>\text{H}_2\bar{\text{T}}</math>, and finally <math>\text{NH}_4\text{HO}</math> in excess.</i>	
FILTRATE	PRECIPITATE	FILTRATE	PRECIPITATE
ALUMINIC OXIDE AND PHOSPHATE. <i>Add <math>\text{H}\bar{\text{A}}</math> in excess.</i>	OF CHROMIC OXIDE AND PHOSPHATE.  Examine for the oxide and phosphate in the way stated in par. 186.	FERRIC NITRATE, FERRIC PHOSPHATE.  <i>Divide the solution into two parts</i>	THE PHOSPHATES AND OXALATES OF THE ALKALINE EARTHS.  <i>Dissolve in <math>\text{HNO}_3</math>, and add solution of <math>\text{HgNO}_3</math>.</i>
FILTRATE Aluminic Oxide. <i>Add <math>\text{Na}_2\text{HPO}_4</math>.</i>	PRECIPITATE Aluminic Oxide. <i>Add <math>\text{Na}_2\text{HPO}_4</math>.</i>	<i>To one part add <math>\text{H}\bar{\text{A}}</math> until the solution possesses the other part <math>\text{NH}_4\text{Cl}</math> and <math>\text{MgSO}_4</math>; then add <math>\text{K}_4\text{FeCy}_6</math>.</i>	FILTRATE Ba, Sr, or Ca, originally in combination with $\bar{\text{O}}$ , and the PHOSPHATES OF the ALKALINE EARTHS, along with the excess of $\text{HgNO}_3$ . <i>Add <math>\text{NH}_4\text{HO}</math> slightly in excess.</i>
		<i>If a blue precipitate is formed after it shows the pre-agitating the fluid and allowing it to stand for some time, it shows the presence of <math>\text{PO}_4</math>.</i>	PRECIPITATE MERCURIUS OXALATE.  <i>Confirm the presence of <math>\bar{\text{O}}</math> by boiling the precipitate in <math>(\text{NH}_4)_2\text{S}</math>; filter, and acidify with <math>\text{H}\bar{\text{A}}</math>; filter, if necessary, and then add to the solution <math>\text{CaSO}_4</math>.</i>
FILTRATE Al as a phosphate.	PRECIPITATE.	<i>NOTE.—To ascertain whether there was any Fe uncombined with <math>\text{PO}_4</math>, add to the original solution <math>\text{NaA}</math>; filter, and to the filtrate add <math>\text{K}_4\text{FeCy}_6</math>.</i>	PRECIPITATE MERCURIUS PHOSPHATE <i>Along with the excess of <math>\text{Hg}_2\text{O}</math>. Boil the precipitate in <math>(\text{NH}_4)_2\text{S}</math>; filter, and to the filtrate add <math>\text{NH}_4\text{Cl}</math> and <math>\text{MgSO}_4</math>.</i>
		<i>If a blue precipitate is formed, it proves that all the Fe did not exist as phosphate.</i>	<i>If a precipitate is formed, <math>\bar{\text{O}}</math> is present.</i>

tion of  $\text{HgNO}_3$  to the  $\text{HNO}_3$  solution, even in the absence of oxalates, owing to the  $\text{HNO}_3$  containing a slight trace of  $\text{HCl}$ .

191. The following is another method for the separation of the members of the fourth group and the phosphates and oxalates which are precipitated along with them by the group reagent; the precipitate produced by  $\text{NH}_4\text{HO}$ , after being well washed, is ignited upon a piece of platinum foil, or in a small crucible; if one or more of the three oxalates (baric, strontic, and calcic) are present, they will be converted by the ignition into *carbonates*; dissolve the ignited precipitate in as small a quantity of boiling dilute  $\text{HCl}$  as possible; if it dissolves with *effervescence*, one or more of the three oxalates are present; examine the solution in this case according to par. 192. If the solution is unattended with effervescence, the three oxalates are absent; examine the solution in this case according to par. 193.

192. When the solution is attended with effervescence, add  $\text{NH}_4\text{HO}$  in excess to the solution, warm, and filter; the filtrate will contain the base or bases originally existing as oxalates; examine for these bases in the way directed in the second group, par. 68; wash the precipitate very well, then dissolve it in as small a quantity of boiling dilute  $\text{HCl}$  as possible; examine the solution according to par. 193.

193. Add  $\text{NH}_4\text{HO}$  the fixed alkalies in excess in the *cold* to the  $\text{HCl}$  solution; if FERRIC PHOSPHATE OR OXIDE, or any of the PHOSPHATES OF THE ALKALINE EARTHS are present, they will be *precipitated*, whilst ALUMINIC and CHROMIC OXIDES and their PHOSPHATES will be retained in *solution*; examine the precipitate according to par. 195, and the solution according to par. 194.

194. *Boil* the fixed alkaline solution for some time; if a precipitate is produced, it is due to the presence of CHROMIC PHOSPHATE OR OXIDE, or both; filter when a precipitate is produced, add to the filtrate, or to the solution, without filtering, when no precipitate has been produced,\* acetic acid in excess; ALUMINIC PHOSPHATE, if present, will be precipitated; add to the filtrate  $\text{NH}_4\text{HO}$  in excess, when  $\text{Al}_2\text{O}_3$ , if present, will be precipitated. Dissolve the chro-

\* If no precipitate is produced on boiling the fixed alkaline solution, a portion of the precipitate produced by the group reagent ought to be examined for chromium, in the way directed at par. 157.

mic precipitate in as small a quantity of boiling dilute HCl as possible, add an *alkaline acetate* in excess; CHROMIC PHOSPHATE, if present, will be precipitated; to the filtrate add  $\text{NH}_4\text{HO}$  in excess; if CHROMIC OXIDE be present, it will be precipitated.

195. After the precipitate produced by the fixed alkali has been well washed, it must be dissolved in as small a quantity of boiling dilute HCl as possible, then add one of the *alkaline acetates* in excess, and *boil* for some minutes; the FERRIC PHOSPHATE and OXIDE (the latter as basic acetate), will be *precipitated*, if present, whilst the PHOSPHATES OF THE ALKALINE EARTHS will remain in *solution*; examine the solution according to par. 196, and examine the precipitate for  $\text{PO}_4$  in the following way: Digest the precipitate in  $(\text{NH}_4)_2\text{S}$  for a few minutes, then filter and examine the filtrate for  $\text{PO}_4$ , according to par. 424. To ascertain whether there was any Fe uncombined with  $\text{PO}_4$ , add to the original solution an *alkaline acetate*; filter and to the filtrate add *potassic ferrocyanide*. If a blue precipitate is formed, it proves that all the Fe *did not* exist as phosphate.

196. To the solution add  $\text{Fe}_2\text{Cl}_6$ , drop by drop; if no precipitate is produced on the addition of the first two drops, the PHOSPHATES OF THE ALKALINE EARTHS are *absent*; if a precipitate is produced, continue the addition of the  $\text{Fe}_2\text{Cl}_6$  until the solution is of a slightly reddish color, then boil until the excess of Fe is removed from the solution by boiling, then filter, and examine the filtrate for Ba, Sr, Ca, Mg, in the usual way.

197. When substances are examined, the nature of which is a sufficient proof that the chromic oxide and phosphate, and the baric and strontic phosphates, and the baric, strontic, and calcic oxalates must be absent, as in the case of soils, natural and artificial manures, etc.,\* the last method may be much simplified;—the precipitate produced by the group reagent need not be ignited, the free alkali need not be added in the cold, and after its addition the mixture may be boiled, in order to hasten the filtration; and lastly, Ca and Mg have only to be sought for.

198. When substances are examined, the nature of which is a sufficient proof that calcic oxalate is the only oxalate, and that calcic and magnesian phosphates are the

\* Guano generally contains oxalate of lime; examine the ammonia precipitate of this manure according to par. 198.

only phosphates of the alkaline earths which can be present, as in the case of *guano, urine, urinary deposits*, etc.,\* a simpler method may be employed for detecting and separating these salts than the one given in Table V.: after having separated them from all the other substances in the way directed in Table V., dissolve the precipitate produced by  $\text{NH}_4\text{HO}$  in the  $\text{H}_2\text{T}$  solution in a small quantity of  $\text{HCl}$ , and to the solution add acetate of soda in excess.  $\text{CaO}$ , if present, will be precipitated, whilst the calcic and magnesian phosphates will remain in solution. Filter, and to the filtrate add  $\text{H}_2\text{O}$ , which will precipitate the Ca existing originally as PHOSPHATE in the state of OXALATE. MAGNESIC PHOSPHATE will be precipitated from this filtrate on the addition of  $\text{NH}_4\text{HO}$  in excess.

199 The BORATES and FLUORIDES of BARYTA, STRONTIA, and LIME are also precipitated by  $\text{NH}_4\text{HO}$ ; but they are not completely precipitated by  $\text{NH}_4\text{HO}$  in the presence of  $\text{NH}_4\text{Cl}$ ; therefore, a portion at least of the bases of these salts will be found as a member of the second group, and the acids in these salts will be discovered in the ordinary examination of the acids; for these reasons we have not included these salts in the group; but it is necessary for the student to know that, when present in considerable quantities, they are in part precipitated by  $\text{NH}_4\text{HO}$ , as otherwise their precipitation along with the members of the 4th group might occasion him much perplexity.

Answers to the following exercises must be written out:—

#### EXERCISES.

87. What change does calcic oxalate undergo on being heated?

88. How would you examine a substance for baric and calcic phosphate?

89. If there were present in an acid solution  $\text{CaO}$ ,  $\text{BaHPO}_4$ ,  $\text{Fe}''''\text{PO}_4$ , and  $\text{Al}''''\text{PO}_4$  and  $\text{NH}_4\text{HO}$ , and  $(\text{NH}_4)_2\text{S}$  were added to it, which of the substances would be precipitated, and in what state would they be precipitated?

90. If there were present in an  $\text{HCl}$  solution  $\text{CaO}$ ,  $\text{Fe}''''\text{PO}_4$ ,  $\text{Al}''''\text{PO}_4$ ,  $\text{CaHPO}_4$ , and sodic acetate in excess

\* Of course in such substances as guano, urine, and urinary deposits, chromic oxide and its phosphate cannot be present.

were added, which of the substances would be precipitated, and in what state would they be precipitated?

91. If you had a solution which could only contain calcic oxalate, calcic phosphate, and magnesia phosphate, devise a speedy method for the examination of these substances.

200. URANIC OXIDE ( $U_2O_3$ ). *Solution of uranic nitrate in water may be employed for the reactions.* This oxide is of a brick-red color, its hydrate is yellow; by ignition it loses part of its oxygen, being converted into  $U_3O_4$ , the color of which is a very dark green, approaching black.  $U_2O_3$  dissolves in acids, forming salts, the solutions of which have a fine yellow color, and redden blue litmus paper.  $H_2S$  converts  $U_2O_3$  into  $UO$ , which attracts O from the air, becoming converted into  $U_2O_3$  again: oxidizing agents have the same effect.

201.  $(NH_4)_2S$  precipitates, from alkaline solution of this oxide, a brownish-colored precipitate, which subsides slowly, and is readily soluble in acids, even in  $HAc$ ;  $NH_4Cl$  promotes the formation of the precipitate.

202. The volatile and fixed alkalis precipitate this oxide from its solutions completely, in the form of a yellow precipitate, which is insoluble in an excess of the reagent.

203.  $(NH_4)_2CO_3$  produces a yellow precipitate, which is soluble in an excess of the reagent, but is deposited again from this solution on boiling. In its behavior with this reagent,  $U_2O_3$  differs from  $Fe_2O_3$ , which it so closely resembles in its other reactions.  $KHCO_3$  or  $NaHCO_3$  produces a yellow precipitate which dissolves readily in an excess of the reagent.

204.  $K_4FeCy_6$  produces in solution of this oxide a fine brown-red precipitate; this is a very delicate test for uranium.

205. "Uranium compounds give a yellow bead in the oxidizing flame, which becomes green in the reducing flame, especially on addition of  $SnCl_2$ . These colors closely resemble those of the iron compounds, but may easily be distinguished, at least if no other coloring metallic oxide is present, by the fact that the uranium bead, when incandescent, emits a bluish-green light, analogous to that which the uranium compounds exhibit when fluorescing. Beads of lead-oxide, stannic acid, and a few other substances, exhibit a similar phenomenon when incandescent, but they do not yield, like uranium compounds, a colored bead on cooling.

206. "Heated gently on the platinum spiral with  $KHSO_4$  the insoluble uranium compounds can be decomposed. The melted mass is powdered with a few particles of crystallized sodic carbonate, and the moistened mass is absorbed by filtering paper. A brown spot is formed by the addition of a drop of  $K_4FeCy_6$  to the moistened paper."—*Bunsen*.

*Characteristic.*—The reactions with the caustic and carbonated alkalis and with  $K_4FeCy_6$ .

207. TITANIC OXIDE OR ANHYDRIDE ( $TiO_2$ ).—This compound, although comparatively a rare substance, occurs in some iron ores, and as it is considered by some to improve the quality of the iron, we have given, on this account, a short description of its properties, and the mode of detecting it.

208. It varies in color according to the mode of preparation; it sometimes appears as a white powder, which, when heated, acquires, during the time it is heated, a yellow tint, and sometimes it appears in the form of small lumps of a reddish-brown color. The acid  $H_2TiO_3$  is white.

The anhydride is insoluble in water and acids, with the exception of concentrated  $\text{H}_2\text{SO}_4$ , which dissolves it with the aid of heat; when fused with  $\text{NaHSO}_4$ , the fused mass dissolves completely in a large quantity of cold water; when fused with  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{TiO}_3$  is formed, which is decomposed by  $\text{H}_2\text{O}$  into an acid salt, insoluble in  $\text{H}_2\text{O}$  but soluble in  $\text{HCl}$  and  $\text{NaHO}$ .

209. The acid in the moist state, and also when dried at a temperature not exceeding  $100^\circ\text{C}$ ., is soluble in dilute acids, especially  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$ . When the acid solutions of it are greatly diluted with water, and boiled for a long time, it,  $\text{H}_2\text{TiO}_3$ , is completely precipitated as a white powder, insoluble in dilute acids; this precipitate possesses the marked property of passing through the filter when washed, unless an acid or  $\text{NH}_4\text{Cl}$  is added along with it. It is precipitated from its acid solutions\* in the form of a milky-white precipitate by the volatile and fixed alkalis and their carbonates, by  $\text{BaCO}_3$  and by  $(\text{NH}_4)_2\text{S}$ ; the precipitate is insoluble in an excess of the precipitant; but if it has been precipitated by any of these reagents in the cold, and washed with cold water it is soluble in dilute  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ .

210. When the solution of titanic acid in  $\text{HCl}$  does not contain too much free  $\text{HCl}$ —when, for example, it has been prepared in such a way that part of the titanate treated by the  $\text{HCl}$  has remained undissolved, and has been filtered from the solution diluted with water—the solution of the acid behaves with the reagents named *a*, *b*, and *c*, in the way described in these paragraphs.

(a) *Infusion of galls* produces in the solution a reddish orange-yellow precipitate of TANNATE OF TITANIC OXIDE.

(b)  $\text{K}_4\text{FeCy}_6$  gives a dense orange-brown precipitate; the precipitate is soluble in an excess of the precipitant.

(c) White precipitates are produced by adding to the solution *dilute sulphuric, arsenic, phosphoric, or tartaric acid* but more especially *oxalic acid*; these precipitates are completely redissolved in an excess of the precipitating acid; and likewise by  $\text{HCl}$ ; the precipitate produced by  $\text{H}_2\text{O}$  is the most insoluble.

211. If a strip of ZINC, IRON, or TIN be introduced into a solution of titanic acid in  $\text{HCl}$ , the solution will become blue; and from this a reddish or violet precipitate will separate, which gradually oxidizes into the white oxide.

212. "Titanic compounds give a colorless bead with microcosmic salt in the oxidizing flame, which turns of a pale amethystine color in the reducing flame. On addition of  $\text{FeSO}_4$  the bead assumes in the reducing flame the peculiar red color of venous blood, whilst in the oxidizing flame the light brown color of  $\text{Fe}_2\text{O}_3$  can be obtained at pleasure. The titanic compounds form with soda a bead, which at first effervesces, and when hot is colorless and transparent, but on cooling becomes opaque. If to the hot bead  $\text{SnCl}_2$  be added, and if it then be heated in the lower reducing flame, a gray mass is formed, which dissolves on heating in  $\text{HCl}$ , yielding a pale amethystine-colored solution."—*Bunsen*.

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\* Not in the presence of tartaric acid, or other non-volatile organic matter.

## FIFTH GROUP.

STANNOUS OXIDE ( $\text{SnO}$ ), STANNIC OXIDE ( $\text{SnO}_2$ ), ANTIMONIOUS OXIDE ( $\text{Sb}_2\text{O}_3$ ), ARSENIOUS ANHYDRIDE ( $\text{As}_2\text{O}_3$ ), ARSENIC ANHYDRIDE ( $\text{As}_2\text{O}_5$ ), AURIC OXIDE ( $\text{Au}_2\text{O}_3$ ), PLATINIC OXIDE ( $\text{PtO}_2$ ).

*Solutions for the reactions.*— $\text{SnCl}_2$ ,  $\text{SnCl}_4$ ,  $\text{As}_2\text{O}_3$ ,  $\text{PtCl}_4$ ,  $\text{AuCl}_3$ , in water;  $\text{SbCl}_3$ ,  $\text{As}_2\text{O}_3$  in dilute  $\text{HCl}$ .\*

213. *Examination for the members of the group.*—Auric and platinic compounds produce reactions so decisive—the former with the tin chlorides (284), and the latter with  $\text{NH}_4\text{Cl}$  (287)—that they may invariably be detected in the presence of all the other metals; they may, therefore, in all cases be sought for in the original solution. The examination of the precipitate produced by the *group reagent*, which must be added as directed at 357, is, therefore, confined to the other members of the group. Six different methods for the analysis of the group precipitate are given.

214. *First method.*—The group precipitate must be well washed, and then treated with a dilute solution of  $\text{NH}_4\text{HCO}_3$ .†  $\text{As}_2\text{S}_3$  is soluble, and  $\text{Sb}_2\text{S}_3$ ,  $\text{SnS}$ ,  $\text{SnS}_2$  are insoluble in  $\text{NH}_4\text{HCO}_3$ ; filter if necessary, and add to the filtrate  $\text{HCl}$  in excess. If a *yellow* precipitate, or a slight yellow color, is produced,  $\text{As}_2\text{S}_3$  is present; the original solution must be examined to ascertain which of the two oxides of As is, or whether both are, present. The substance insoluble in  $\text{NH}_4\text{HCO}_3$ , after having been dried, must be mixed with three parts of fused  $\text{NH}_4\text{NO}_3$ ,‡ and the mixture projected in small portions at a time into a porcelain crucible, containing two parts of  $\text{NH}_4\text{NO}_3$  in a state of liquefaction. The ignition should be continued

\* As no table is given with this group the student ought to perform the experiments given under the individual members before attempting the analysis of the group.

† The solution is prepared by dissolving one ounce of  $\text{NH}_4\text{HCO}_3$  in twelve ounces by measure of water; the precipitate must be agitated for a few seconds only with the solution, and then quickly filtered.

‡ When the amount of precipitate is so small that little or nothing can be detached from the filter, the precipitate as well as the filter, after having been cut into small pieces, must be mixed up with the ammoniac nitrate, and subsequently projected into the crucible.

for a short time after all fuming has ceased, and the residue, when cold, must be treated with a *saturated* solution of  $\text{H}_2\text{T}$ ; if complete solution takes place,  $\text{Sb}_2\text{O}_3$  only can be present; but if a portion remains undissolved, one or both of the *tin* oxides are probably present. Filter the  $\text{H}_2\text{T}$  solution when necessary, and add to the filtrate  $\text{HCl}$  and  $\text{H}_2\text{S}$  in excess; if an *orange-red* precipitate is formed,  $\text{Sb}_2\text{O}_3$  is present. The substance insoluble in  $\text{H}_2\text{T}$  must be examined for  $\text{Sn}$  by fusing it with  $\text{Na}_2\text{CO}_3$  and  $\text{KCy}$ , as directed at par. 236.

215. *Second method.*—Dry the precipitate, then treat it with boiling concentrated  $\text{HCl}$ ;  $\text{Sb}_2\text{S}_3$ ,  $\text{SnS}$ , and  $\text{SnS}_2$  will dissolve with decomposition, whilst  $\text{As}_2\text{S}_3$  will remain undissolved. Add a little water to the  $\text{HCl}$  solution, and pour it into a platinum crucible or lid, and introduce into it a piece of *pure* zinc, the  $\text{Sn}$  and  $\text{Sb}$  are reduced to the metallic state, and the latter blackens the platinum; when  $\text{H}$  ceases to be evolved remove the zinc, washing into the crucible or lid any reduced metal adhering to it, then free the reduced metal from the  $\text{ZnCl}_2$  by washing, boil it in strong  $\text{HCl}$ ,  $\text{Sn}$  will dissolve, whilst  $\text{Sb}$  will remain undissolved. Dilute the  $\text{HCl}$  solution a little, and then test it for  $\text{Sn}$  by adding to it  $\text{HgCl}_2$  (235), or a mixture of  $\text{Fe}_2\text{Cl}_6$  and  $\text{K}_6\text{Fe}_2\text{Cy}_{12}$  (234); dissolve the portion of the metal insoluble in  $\text{HCl}$  in aqua regia, and test it for  $\text{Sb}$  by passing  $\text{H}_2\text{S}$  through the solution. Dissolve the portion of the sulphide insoluble in  $\text{HCl}$  in boiling  $\text{HNO}_3$ , evaporate nearly to dryness, add cold water, and test for  $\text{H}_3\text{AsO}_4$  by adding  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{HO}$ , and  $\text{MgSO}_4$  (277), or by adding  $\text{AgNO}_3$  (275).

216. *Third method.*—Mix the dried *sulphides* with an equal quantity of  $\text{Na}_2\text{CO}_3$  and a like quantity of  $\text{NaNO}_3$ ; transfer the mixture gradually into a porcelain crucible containing twice the quantity of  $\text{NaNO}_3$  *in a state of fusion*; when the deflagration is over\* allow the crucible to cool; treat the fused mass with *cold* water and filter; wash the insoluble portion with equal parts of alcohol and water; filter the washings and mix them with the filtrate; add  $\text{HNO}_3$  to the solution until it is distinctly acid; heat to expel  $\text{CO}_2$  and  $\text{N}_2\text{O}_3$  and test for  $\text{H}_3\text{AsO}_4$  as directed in the

\* The heat must not be too high nor continued too long, otherwise the  $\text{NaNO}_3$  will be decomposed and caustic soda formed; and this latter will form with  $\text{SnO}_2$  sodio stannate which will dissolve in the water.



second method; heat the insoluble residue with HCl; transfer to a platinum vessel, and test for Sn and Sb as directed in preceding par.

217. *Fourth method.*—Dissolve the sulphides in  $K_2S$ ; add a concentrated solution of  $SO_2$  in large excess, and digest the mixture in the water-bath for some time, then boil until all  $SO_2$  is expelled, and afterwards filter; the filtrate will contain the  $As_2O_3$ , if present; test for it by passing  $H_2S$  into the solution; dissolve the insoluble portion in HCl and test it for Sb and Sn as in the second method.

218. *Fifth method.*—Dissolve the precipitated sulphides in as small a quantity of hot aqua regia as possible; introduce the solution into a hydrogen apparatus, along with some Zn and diluted  $H_2SO_4$ . The gas bottle must be connected with a second one containing a dilute solution of  $Pb2A$ ,\* through which the gas in passing is freed from any HCl and  $H_2S$ . The exit tube from the wash bottle dips into a precipitating glass or test tube containing a solution of  $AgNO_3$ . If a precipitate is produced continue the transmission through the solution as long as it continues to be produced; then filter, carefully neutralize the  $HNO_3$  in the filtrate with  $NH_4HO$ ; the characteristic yellow  $Ag_3AsO_4$  is precipitated. If the gas has passed through the solution for a long time, the solution may contain no Ag. If, therefore, after neutralizing it no yellow precipitate is formed, add a drop or two of  $AgNO_3$  to it. Wash the silver precipitate thoroughly with boiling water, and then boil it with a solution of  $H_2T$ . Filter and acidify the filtrate with HCl, and pass  $H_2S$  through it; if Sb be present orange-colored  $Sb_2S_3$  will be produced. In order to detect Sn the metallic precipitate is washed off the Zn in the gas bottle and boiled in HCl; then diluted with a little  $H_2O$ , and tested for Sn by adding a solution of  $HgCl_2$  (235).

219. *Sixth method.*—"If in a mixture of these three sulphides, containing only traces of Sb and Sn, they are separated according to the ordinary rules of qualitative analysis by dissolving in alkaline sulphides and reprecipitation with acids, the detection of these two metals by the regular tests is extremely uncertain and troublesome. According to the following method the detection of these metals is rendered easy and certain when the proportion

\* A tube containing glass-splinters, moistened with a solution of  $Pb(A)_2$ , may be employed in place of the wash-bottle.

of Sn is only a few thousandths, and that of the Sb only a few hundredths, of the total weight of the mixture.

220. "Three decigrammes of the sulphides are roasted on a curved piece of glass small enough to be altogether surrounded by the flame, and the residue, weighing only a few milligrammes, is scraped together with the knife. The moistened mass is then collected on the end of a thread of asbestos and a strong metallic film obtained on the test tube. In order to prevent the deposition of any carbon with the metals, which would act injuriously in the subsequent operations, the upper reducing flame is made so small that the luminous point is only just visible. The film is next dissolved in a drop or two of  $\text{HNO}_3$  in the curved rim (fig. 3) of the *Plate*, and the solution evaporated below its boiling-point by gently warming and blowing, so as to obtain the solid residue in as small a space as possible. A drop of neutral silver solution is now brought on to the residue at the moment when it becomes solid; and on blowing with ammoniacal air a characteristic black stain is formed, whilst the reaction of As is also generally noticed.

221. "In order to detect Sn, a few scarcely visible particles of the roasted sulphides are fused on to a borax bead which has been very slightly tinted with cupric oxide. If the bead is now brought into the lower reducing flame, it becomes a ruby-red color from reduced cuprous oxide. If the oxide be present in too large a quantity, the bead can be obtained transparent by the process described under the reactions of the copper compounds. This reaction can only be obtained in the lower reducing flame of the non-luminous gas-lamp, as in the ordinary blowpipe flame, the cupric oxide is reduced to cuprous oxide without the presence of tin-salt,"—*Bunsen*.

PROPERTIES OF THE METALS, THE OXIDES, THE SULPHIDES, THE CHLORIDES, AND THE HYBRIDES OF As AND Sb.

222. *The metals*.—As volatilizes at a dull red heat without previous fusion, its vapor is colorless and has a garlic odor. Sb melts at  $432^\circ \text{C}$ ., and at a bright red heat volatilizes slowly, which is facilitated by transmitting a current of H over it. Sn melts at  $228^\circ \text{C}$ ., and boils at a white heat; Au melts at above  $1040^\circ \text{C}$ .; Au and Sn are but slightly volatile in the heat of a furnace. Pt does not melt in the strongest forge fire, but it is fused and volatilized by

the voltaic current, and in the oxyhydrogen blowpipe flame. Au and Pt suffer no change by exposure to air and moisture at any temperature. The other three metals undergo no change at ordinary temperatures in dry air, neither in moist air does Sb suffer any change, but Sn tarnishes, and As slowly oxidizes; they all three unite with O if heated in the air, and at high temperatures burn with a brilliant light,  $\text{As}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_3$ , and  $\text{SnO}_2$  being formed. Sb and Sn decompose steam at a red heat. As decomposes it only slightly. Pt is not acted upon by any single acid, and selenic acid is the only one that acts on Au. HCl does not attack Sb, and has little action on As, but if heated it dissolves Sn,  $\text{SnCl}_2$  being formed and H evolved. Dilute  $\text{H}_2\text{SO}_4$  is without action on them, but boiling concentrated  $\text{H}_2\text{SO}_4$  acts on them,  $\text{SO}_2$  being evolved and  $\text{As}_2\text{O}_3$ ,  $\text{Sb}_2(\text{SO}_4)_3$ ,  $\text{Sn}(\text{SO}_4)_2$  being formed; in the last case there is also a separation of S. Dilute  $\text{HNO}_3$  converts As and Sb with the aid of heat into  $\text{As}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_3$ . The concentrated and boiling acid converts them into  $\text{As}_2\text{O}_5$  and  $\text{Sb}_2\text{O}_5$ .  $\text{HNO}_3$ , if its sp. gr. is 1.5, does not act on Sn, but if it be diluted to 1.3 it acts violently upon it, converting it into metastannic acid ( $\text{H}_2\text{Sn}_3\text{O}_{11}, 4\text{H}_2\text{O}$ ), nitrous fumes are evolved, ammonia is also formed owing to the decomposition of  $\text{H}_2\text{O}$ . Aqua regia attacks all the five metals, converting them into  $\text{PtCl}_4$ ,  $\text{AuCl}_3$ ,  $\text{SnCl}_4$ ,  $\text{SbCl}_5$ , and  $\text{As}_2\text{O}_5$ . Sb, As, and Sn, combine readily with Cl, Br, I, P, and S; with some at ordinary, with others of them at higher temperatures. Au combines directly with Cl, Br, and F, without the aid of heat, and with P when heated; dry Cl is without action on Pt; P and As combine with it when heated, forming phosphides and arsenides, which are very fusible; S also combines with spongy Pt, with the aid of heat. Chlorine water acts slowly upon Pt, and it converts Au into  $\text{AuCl}_3$ . The caustic alkalis do not affect Au, but the hydrates of the alkalis and alkaline earths, especially  $\text{LiHO}$  and  $\text{BaH}_2\text{O}_2$ , act on Pt if heated to redness with it in the air. It is even attacked at high temperatures by  $\text{KHSO}_4$ . As and Sn are also attacked by these hydrates at high temperatures;\* in the case of Sn a metastannate is formed and H evolved; and in the case of As an arsenite and an arsenide are formed and H evolved. As and Sb, if in the form of an alloy, may be completely separated by heating the com-

\* When As is boiled in a strong solution of KHO, arsenite of potash is formed and H evolved.

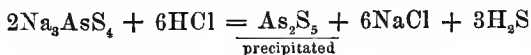
pound to low redness in a stream of  $\text{CO}_2$ , the As volatilizes whilst the Sb remains. Sb is the only metal which can be separated completely from As in this way, with all other metals a part of the As always remains combined. In their chemical relations these metals exhibit rather a chlorous than a basylous character, so that their oxides tend to unite with bases rather than with acids.

223. *The oxides.*— $\text{SnO}$ ,  $\text{SnO}_2$ ,  $\text{PtO}_2$ ,  $\text{As}_2\text{O}_3$  may be obtained by igniting with care their hydrates;  $\text{As}_2\text{O}_5$  may be obtained by burning As in air or O, or by roasting arsenical ores;  $\text{Sb}_2\text{O}_3$  by burning Sb in air;  $\text{Au}_2\text{O}_3$  by adding to a solution of  $\text{AuCl}_3$   $\text{MgO}$ , and then dissolving out the  $\text{MgO}$  with  $\text{HNO}_3$ .\*  $\text{Au}_2\text{O}_3$  and  $\text{PtO}_2$  are completely decomposed below a red heat, and  $\text{As}_2\text{O}_5$  is resolved somewhat above its melting point into  $\text{As}_2\text{O}_3$  and O. On being heated in air,  $\text{SnO}$  and  $\text{Sb}_2\text{O}_3$  are converted into  $\text{SnO}_2$  and  $\text{Sb}_2\text{O}_4$ ;  $\text{PtO}_2$  and  $\text{Au}_2\text{O}_3$  are decomposed;  $\text{As}_2\text{O}_5$  is converted into  $\text{As}_2\text{O}_3$ ;  $\text{SnO}_2$  and  $\text{As}_2\text{O}_3$  are unchanged.  $\text{As}_2\text{O}_3$ ,  $\text{As}_2\text{O}_5$ ,  $\text{SnO}$ ,  $\text{SnO}_2$  and  $\text{Sb}_2\text{O}_3$  are reduced to the metallic state on being heated in a current of H or CO, or if mixed with C or KCy; in the latter case potassic cyanate is formed.  $\text{SnO}$ ,  $\text{SnO}_2$ , and  $\text{Sb}_2\text{O}_3$ , on being heated with S, are converted into the corresponding sulphides,  $\text{SO}_2$  being evolved;  $\text{As}_2\text{S}_3$  is formed on heating  $\text{As}_2\text{O}_3$  with S, but a varying amount of  $\text{As}_2\text{O}_3$  always escapes unconverted. If the oxides of Sn, Sb, and As are heated with  $\text{NH}_4\text{Cl}$ , chlorides of the metals are formed which volatilize; they are likewise converted into chlorides when heated in an atmosphere of Cl.  $\text{PtO}_2$  and  $\text{Au}_2\text{O}_3$  are reduced to the metallic state on being heated in an atmosphere of Cl. If As and Sb, or their sulphides, are diffused through a solution of KHO, and Cl conducted into the fluid, they are converted into arsenic and antimonious acids, which combine with some of the potash;  $\text{SnO}$  is converted into  $\text{SnO}_2$  by adding to its solution Cl.  $\text{SnO}$ , on being boiled in a small quantity of solution of KHO, is decomposed into Sn and  $\text{SnO}_2$ . The hydrates of these oxides may be obtained as follows:  $\text{Sb}_2\text{O}_3 \cdot \text{H}_2\text{O}$  and  $2\text{SnO} \cdot \text{H}_2\text{O}$  by adding solutions of their chlorides to a solution of  $\text{Na}_2\text{CO}_3$ ;  $\text{H}_2\text{SnO}_3$  by adding to a solution of  $\text{SnCl}_4$  an insoluble carbonate, as  $\text{CaCO}_3$ , in quantity insufficient for the entire

\* Magnesie aurate is precipitated, and on the addition of  $\text{HNO}_3$  to the precipitate the  $\text{MgO}$  is dissolved, and the auric oxide is left in the anhydrous state if strong acid be employed, but in the hydrous state if the acid employed be weak.

decomposition of the chloride;  $\text{PtO}_2$ ,  $2\text{H}_2\text{O}$  by adding to a solution of platanic nitrate a solution of  $\text{Na}_2\text{CO}_3$  in quantity insufficient for its complete decomposition;  $\text{H}_3\text{AsO}_3$  by evaporating the arsenic solution obtained by oxidizing  $\text{As}_2\text{O}_3$  with  $\text{HNO}_3$ ;  $\text{H}_3\text{AsO}_3$  is supposed to exist in solution, but it has never yet been isolated. Auric hydrate is obtained as directed in the note, page 104.  $\text{As}_2\text{O}_3$ ,  $\text{As}_2\text{O}_5$ , and  $\text{H}_3\text{AsO}_4$  are white; they are soluble in  $\text{H}_2\text{O}$ .  $\text{SnO}$  is black,  $2\text{SnO}$ ,  $\text{H}_2\text{O}$  is white; they are insoluble in  $\text{H}_2\text{O}$ . The hydrate is dissolved readily by acids, the anhydride is more slowly acted upon by them, the hydrate is soluble in the fixed alkalies, but if boiled with them is decomposed,  $\text{SnO}_2$  remaining in solution, and  $\text{Sn}$  separating.  $\text{SnO}_2$  is of a light straw color, the hydrate is white; they are insoluble in  $\text{H}_2\text{O}$ ; the anhydride is insoluble in acids, but forms soluble compounds with the alkalies; the hydrate is soluble in acids and the fixed alkalies.  $\text{Sb}_2\text{O}_3$  and its hydrate are white; they are insoluble in  $\text{H}_2\text{O}$ , but soluble in  $\text{HCl}$  and  $\text{H}_2\text{T}$ ; their solution in this latter acid distinguishes them from the other anhydrous and hydrous oxides of the group; they are also readily soluble in solution of the fixed alkalies.  $\text{HNO}_3$ , or fusion with nitrates, converts  $\text{Sb}_2\text{O}_3$  into a higher oxide.  $\text{Au}_2\text{O}_3$  is of a deep brown color; its hydrate is somewhat lighter in color.  $\text{PtO}_2$  and its hydrate are reddish-brown. The auric and platinic oxides and their hydrates are readily soluble in  $\text{HCl}$ , but dissolve with difficulty in the oxygen acids.

224. The *sulphides* are formed, and in the amorphous state, on passing  $\text{H}_2\text{S}$  into a solution of their salts containing some free mineral acid,\* with the exception of  $\text{As}_2\text{S}_3$ , as  $\text{As}_2\text{S}_5$ , with separation of sulphur, and not  $\text{As}_2\text{S}_5$ , is formed on passing  $\text{H}_2\text{S}$  into acid solutions of  $\text{As}_2\text{O}_5$ . The amorphous  $\text{Sb}_2\text{S}_3$ ,  $\text{SnS}$ , and  $\text{SnS}_2$ , obtained in this manner, are hydrated.  $\text{As}_2\text{S}_5$  may be formed by adding  $\text{HCl}$  or other acid to a dilute aqueous solution of  $\text{Na}_3\text{AsS}_4$ , or any soluble sulph-arsenic salt. The following is the reaction:—



$\text{Sb}_2\text{S}_3$  may be obtained in crystals by melting together at a red heat a mixture of  $\text{S}$  and  $\text{Sb}_2\text{O}_3$ .  $\text{SnS}$  may be obtained crystalline by heating  $\text{Sn}$ , in a finely-divided state, with  $\text{S}$ .

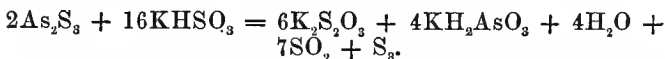
\*  $\text{Au}_2\text{S}_3$  is precipitated by  $\text{H}_2\text{S}$  from cold solutions of  $\text{AuCl}_3$ , but if the solution of  $\text{AuCl}_3$  is boiling  $\text{Au}_2\text{S}$  is precipitated.

$\text{SnS}_2$  may be obtained crystalline by heating a mixture of tin-filings, S, and  $\text{NH}_4\text{Cl}$ , or Hg, slowly to redness in a glass retort or loosely-covered flask.  $\text{SnS}_2$  cannot be obtained by simply heating Sn and S, because the union is attended with such a development of heat that  $\text{SnS}_2$  is resolved into  $\text{SnS}$  and S. A volatile substance, as  $\text{NH}_4\text{Cl}$  or Hg, is added to lower the temperature by rendering *latent* some of the heat evolved. The sulphides of this group are insoluble in  $\text{H}_2\text{O}$ , but soluble in the alkalies and alkaline sulphides. These sulphides possess acid characters; they, therefore, combine with the alkaline sulphides, which are basic, and form sulphur salts. When dissolved in the alkalies an oxygen, as well as a sulphur salt, is formed, thus:—



The solutions of these sulphides in the alkalies and alkaline sulphides are decomposed by the stronger acids, the sulphides reprecipitating, an alkaline salt of the acid added being formed, and when alkaline sulphides are employed  $\text{H}_2\text{S}$  being evolved. The members of this group are not precipitated by  $\text{H}_2\text{S}$  from alkaline solutions. Heated out of contact of the air,  $\text{Au}_2\text{S}_3$  is decomposed into its elements,  $\text{PtS}_2$  and  $\text{SnS}_2$  are converted into the protosulphides, S being given off,  $\text{Sb}_2\text{S}_3$ ,  $\text{As}_2\text{S}_3$ , and  $\text{As}_2\text{S}_5$  melt below a red heat, and volatilize unchanged at a higher temperature. Heated in air,  $\text{Au}_2\text{S}_3$  and  $\text{PtS}_2$  yield Au, Pt, and  $\text{SO}_2$ ,  $\text{SnS}$  and  $\text{SnS}_2$  yield  $\text{SnO}_2$  and  $\text{SO}_2$ ,  $\text{As}_2\text{S}_5$  and  $\text{As}_2\text{S}_3$  yield  $\text{As}_2\text{O}_3$ , and  $\text{SO}_2$ ,  $\text{Sb}_2\text{S}_3$  is converted into a fusible mixture of  $\text{Sb}_2\text{O}_3$  and  $\text{Sb}_2\text{S}_3$ , which is of a red color, and constitutes the commercial glass of antimony. Heated in a current of Cl,  $\text{PtS}_2$  and  $\text{Au}_2\text{S}_3$  are decomposed, Pt and Au remaining,  $\text{As}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{SnS}$ , and  $\text{SnS}_2$ , are converted into  $\text{AsCl}_3$ ,  $\text{SbCl}_3$ , and  $\text{SnCl}_4$ , chloride of sulphur being also formed.  $\text{Au}_2\text{S}_3$ ,  $\text{PtS}_2$ ,  $\text{Sb}_2\text{S}_3$ , and  $\text{SnS}$ , are reduced, the latter only slowly, when heated in a current of H;  $\text{As}_2\text{S}_3$  is only partly reduced by H. The sulphides of As, Sn, and Sb are converted into their highest oxides on being fused with  $\text{NaNO}_3$  and  $\text{Na}_2\text{CO}_3$ ; the fused mass contains, if all these sulphides were present,  $\text{SnO}_2$ , sodic arseniate and antimoniate, with sodic, sulphate, carbonate, nitrate, and nitrite.  $\text{Sb}_2\text{S}_3$  and  $\text{As}_2\text{S}_3$ , when heated in a current of steam, are partially oxidized, a sublimate composed of the oxide and sulphide in each case being formed, and  $\text{H}_2\text{S}$  evolved; if recently precipitated  $\text{Sb}_2\text{S}_3$  and  $\text{As}_2\text{S}_3$  are boiled in  $\text{H}_2\text{O}$  for some

time, a small portion becomes decomposed,  $\text{Sb}_2\text{O}_3$  and  $\text{As}_2\text{O}_3$  being formed, and dissolved in the water, whilst  $\text{H}_2\text{S}$  is evolved. Dry  $\text{HCl}$  gas decomposes  $\text{Sb}_2\text{S}_3$ , but not  $\text{As}_2\text{S}_3$ ; the  $\text{SbCl}_3$  which is formed is very volatile in a current of the  $\text{HCl}$  gas. Recently precipitated  $\text{As}_2\text{S}_3$  dissolves in  $\text{KHSO}_3$  (the sulphides of  $\text{Sn}$  and  $\text{Sb}$  do not); if the solution is heated,  $\text{SO}_2$  and  $\text{S}$  are set free, and there remain in solution  $\text{K}_2\text{S}_2\text{O}_3$  and  $\text{KH}_2\text{AsO}_3$ ; the following is the reaction:—

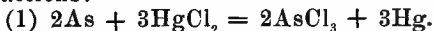


$\text{Sb}_2\text{S}_3$  is decomposed by  $\text{C}$  with heat,  $\text{Sb}$  and  $\text{CS}_2$  being formed, but  $\text{As}_2\text{S}_3$  is not. If vapor of  $\text{As}_2\text{S}_3$  or  $\text{As}_2\text{S}_5$  be passed over heated  $\text{Fe}$  or  $\text{Ag}$ , or other metals, they are decomposed, the  $\text{S}$  combines with the heated metal, and the  $\text{As}$  is set free, which also combines with the reducing metal if it be in excess.  $\text{Sn}$ ,  $\text{Fe}$ ,  $\text{Cu}$ , and other metals, decompose  $\text{Sb}_2\text{S}_3$  at a red heat by combining with the  $\text{S}$ , the liberated  $\text{Sb}$  combines with the reducing metal if it be in excess. If the sulphides of  $\text{As}$ ,  $\text{Sn}$ , and  $\text{Sb}$ , are fused with  $\text{KCy}$ , the metals are obtained, and potassic sulphocyanide is formed. The arsenic sulphides are soluble in  $\text{NH}_4\text{HO}$  and in solutions of  $\text{NH}_4\text{HCO}_3$ , whilst the antimony and tin sulphides are almost insoluble in these reagents. *The color of the sulphides and their solubility in acids:* Crystallized  $\text{Sb}_2\text{S}_3$  is *bluish-black*, the hydrated amorphous  $\text{Sb}_2\text{S}_3$  is *orange-red*, whether in the crystallized or amorphous state it is insoluble in dilute acids, but concentrated  $\text{HCl}$  dissolves it,  $\text{SbCl}_3$  and  $\text{H}_2\text{S}$  being formed; concentrated  $\text{H}_2\text{SO}_4$  decomposes it, yielding  $\text{SO}_2$ ,  $\text{S}$  and a sulphate of  $\text{Sb}_2\text{O}_3$ ; concentrated  $\text{HNO}_3$  also decomposes it. Crystallized and amorphous  $\text{As}_2\text{S}_3$ , also called orpiment,\* is lemon-yellow, concentrated and boiling  $\text{HCl}$  decomposes it only very slightly;  $\text{HNO}_3$  decomposes it,  $\text{H}_3\text{AsO}_4$  and  $\text{H}_2\text{SO}_4$  being formed; it is also decomposed by aqua regia.  $\text{SnS}$  in the crystalline form is bluish-gray, the hydrated amorphous  $\text{SnS}$  is chocolate-brown; it is insoluble in dilute acids; it dissolves in boiling  $\text{HCl}$ ; boiling  $\text{HNO}_3$  converts it into insoluble hydrate of metastannic acid.  $\text{SnS}_2$  obtained in the dry way is a beautiful flaky compound, which is known under the name of mosaic gold; hydrated amorphous  $\text{SnS}_2$  is faintly yellow; aqua regia is the only acid

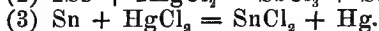
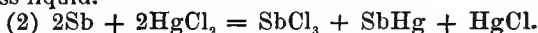
\* Realgar is a sulphide of arsenic, its formula is  $\text{As}_2\text{S}_2$ .

which decomposes mosaic gold, but the hydrated sulphide is not only decomposed by that acid, but also by boiling HCl, and also by concentrated HNO<sub>3</sub>, which converts it into insoluble hydrate of metastannic acid. PtS<sub>2</sub> is blackish-brown, and Au<sub>2</sub>S<sub>3</sub> is black; they are not attacked by HNO<sub>3</sub> or by HCl, but they are dissolved by aqua regia.

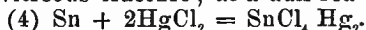
225. *The chlorides.*—AsCl<sub>3</sub>,\* SbCl<sub>3</sub>, SnCl<sub>2</sub>, and SnCl<sub>4</sub> may be obtained in the *anhydrous state* by distilling a mixture of the metals and HgCl<sub>2</sub>. The following are the reactions:—



The AsCl<sub>3</sub> passes over into the receiver as an oily colorless liquid.



The SnCl<sub>2</sub> remains behind as a gray brilliant mass, with a vitreous fracture; at a dull red heat it may be distilled.



On the application of heat, SnCl<sub>4</sub> distils over as colorless liquid. AsCl<sub>3</sub>, SbCl<sub>3</sub>,† and SnCl<sub>4</sub>, may also be prepared by passing a current of Cl over the metals or the sulphides, or by heating stannic or antimonious sulphate with NaCl, and by heating As<sub>2</sub>O<sub>3</sub> with HSO<sub>4</sub> and NaCl. AsCl<sub>3</sub> is a dense, transparent, oily, and volatile liquid, which does not solidify at 18° C., and boils about 132° C. It evaporates in the air at ordinary temperatures. SbCl<sub>3</sub> is a colorless, fusible, volatile solid, which is crystallizable and deliquescent; from its ready fusibility it was formerly known under the name of *butter of antimony*. SnCl<sub>2</sub> is a white, frequently gray, solid, fusible, and volatile at a high heat. SnCl<sub>4</sub> is a transparent, colorless fluid, which does not congeal at -29° C., and boils at 121° C.; it emits dense white fumes when exposed to the air, it absorbs water rapidly from the air, forming a terhydrate SnCl<sub>4</sub> · 3H<sub>2</sub>O. These four chlorides are decomposed by H<sub>2</sub>O, AsCl<sub>3</sub>, if much water is added, is decomposed into As<sub>2</sub>O<sub>3</sub> and HCl, but if only a small quantity is added, into (AsCl<sub>3</sub>, As<sub>2</sub>O<sub>3</sub>) and HCl; SbCl<sub>3</sub> is soluble in a small quantity of H<sub>2</sub>O, but in a large quantity it is decomposed into (SbCl<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>,‡) and HCl; if tartaric is added to the solution this decomposi-

\* There is no other compound of As and Cl known.

† If the Sb is kept in excess, SbCl<sub>3</sub> is formed; but if the Cl is in excess, SbCl<sub>5</sub> is produced.

‡ By continued washing with water the chloride in these two compounds becomes removed and Sb<sub>2</sub>O<sub>3</sub> only remains.



tion is prevented. If hot water be added to a hot solution of  $\text{SbCl}_3$  in  $\text{HCl}$ , it is decomposed into  $(2\text{SbCl}_3, 5\text{Sb}_2\text{O}_3^*)$ , formerly called *powder of Algaroth*, and  $\text{HCl}$ .  $\text{SnCl}_2$  is decomposed, if mixed with a large quantity of water, into  $(\text{SnCl}_2, \text{SnO}, 2\text{H}_2\text{O})$  and  $\text{HCl}$ .  $\text{SnCl}_4$  is readily soluble in a small quantity of water, but it is decomposed if much water be added into  $\text{H}_2\text{SnO}_3$  and  $\text{HCl}$ ; the precipitate of the antimony, stannous and stannic compounds is prevented if  $\text{HCl}$  be added along with the water. In the hydrated state  $\text{SnCl}_2$  is obtained by dissolving  $\text{Sn}$  in  $\text{HCl}$ , the solution is usually effected in copper vessels on a large scale, since the voltaic opposition of the two metals favors the solution of the  $\text{Sn}$ ; it crystallizes on evaporating the liquid in prismatic needles, the formula being  $\text{SnCl}_2, 2\text{H}_2\text{O}$ . A solution of  $\text{SnCl}_4$  may be prepared by dissolving stannic hydrate in  $\text{HCl}$ , or by treating a solution of  $\text{SnCl}_2$  with  $\text{Cl}$  or by mixing  $\text{SnCl}_2$  with  $\text{HCl}$  and treating it with  $\text{HNO}_3$ ; when its aqueous solution is mixed with one of the alkaline sulphates, hydrated stannic oxide is precipitated thus:—

$\text{SnCl}_4 + 4\text{Na}_2\text{SO}_4 + 4\text{H}_2\text{O} = \text{SnO}_2, 2\text{H}_2\text{O} + 4\text{NaCl} + 4\text{NaHSO}_4$ . Hydrated  $\text{SbCl}_3$  is obtained in solution by dissolving  $\text{Sb}_2\text{O}_3$  or  $\text{SbCl}_3$  in  $\text{HCl}$ , the addition of tartaric acid to the solution prevents its decomposition by water; by evaporating the solution of  $\text{Sb}$  in  $\text{HCl}$  anhydrous  $\text{SbCl}_3$  is obtained.  $\text{As}_2\text{O}_3$  dissolves copiously in  $\text{HCl}$ ; and if  $\text{As}_2\text{O}_3$  or one of its salts is distilled with  $\text{HCl}$  of at least 1.1 density,  $\text{AsCl}_3$  passes over with the aqueous acid,  $\text{As}$  may by this means be separated from most other metals and from organic matter; and the reaction explains the presence of  $\text{As}$  in hydrochloric acid made with oil of vitriol containing  $\text{As}$ ; dilute solutions of  $\text{As}_2\text{O}_3$  in  $\text{HCl}$  may be evaporated below  $100^\circ \text{C}$ . without any  $\text{AsCl}_3$  volatilizing; but if the mixture be distilled to dryness in a retort, the  $\text{AsCl}_3$  passes over with the last portions of the acid liquid.  $\text{SbCl}_3$  combines with  $\text{HCl}$  and other chlorides, especially the alkaline chlorides, the general formula for which is  $(\text{M}'\text{Cl})_3 \text{SbCl}_3$ .  $\text{SbCl}_3$  is employed for bronzing gun-barrels to prevent them rusting, the iron decomposes  $\text{SbCl}_3$  and there is formed on the iron a covering of  $\text{Sb}$ .  $\text{SnCl}_2, 2\text{H}_2\text{O}$  in crystals or in solution absorbs oxygen on exposure to the air, and forms a mixture of  $\text{SnCl}_4$  and an

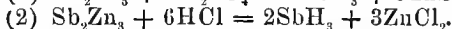
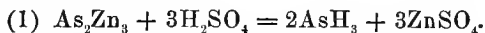
\* By continued washing with water the chloride in these two compounds becomes removed and  $\text{Sb}_2\text{O}_3$  only remains.

oxychloride;\*  $\text{SnCl}_2$  has a strong attraction for Cl and for O, and is therefore a powerful reducing agent; it reduces gold, silver, and mercury salts to the metallic state; it converts ferric and cupric salts into ferrous and cuprous ones; it reduces chromic, manganic, arsenic, antimonie acids, etc., and the higher oxides of Pb and Bi, etc., into lower oxides; it reduces nitric acid to nitric or nitrous oxide, hypochlorous acid to chlorine; it deprives sulphurous acid of its oxygen; it converts indigo-blue into indigo-white; it is extensively employed as a mordant by the dyer and calico-printer under the name of *salts of tin*, and they also employ it for deoxidizing indigo and ferric and manganic oxides. It forms double chlorides with many of the chlorides of the alkalies and alkaline earths.  $\text{SnCl}_4$  forms double salts with the soluble chlorides; the double salt  $2\text{NH}_4\text{Cl}, \text{SnCl}_4$  is the *pink salt* of the dyer; an impure  $\text{SnCl}_4$  is used by dyers under the name *nitro-muriate of tin*, *composition*, *physic*, or *tin solution*, it is used for brightening and fixing red colors.  $\text{PtCl}_4$  and  $\text{AuCl}_3$  are obtained by dissolving the metals in aqua regia, and evaporating the solution to dryness, the former by steam heat, and the latter at a temperature not exceeding  $250^\circ \text{C}$ .; in each case a red deliquescent mass is obtained, which is soluble in water, in alcohol and ether; these chlorides combine with other chlorides, forming double salts; they combine with most of the chlorides of the organic bases, they are therefore employed to determine the combining number of organic alkalies. They both give off Cl when heated, but Pt retains Cl much more tenaciously than Au.  $\text{SO}_2$  and alkaline sulphites reduce  $\text{PtCl}_4$  to  $\text{PtCl}_2$ , but those reagents precipitate Au from  $\text{AuCl}_3$ ; this latter chloride is easily reduced by many substances, for instance by P, by most metals, by *ferrous salts*, by oxalates, by  $\text{As}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_3$ , by many vegetable and animal substances. When Sn is digested in a neutral solution of  $\text{AuCl}_3$ , or a mixture of  $\text{SnCl}_2$  and  $\text{SnCl}_4$ , very much diluted, is added by degrees to a neutral solution of  $\text{AuCl}_3$ , a flocculent purple deposit called *purple of Cassius* is obtained. "The nature of this compound has been the subject of much discussion; Berzelius considered that it consists of a hydrated double stannate of gold and tin ( $\text{Sn}''\text{Au}_2\text{Sn}_2\text{O}_8, 4\text{H}_2\text{O}$ ); it is decom-

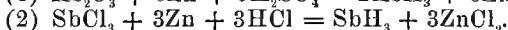
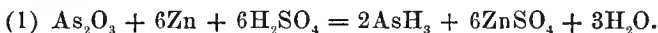
\* The decomposition may be prevented and the solution kept clear, by the addition of  $\text{HCl}$ ,  $\text{HT}$ , or  $\text{NH}_4\text{Cl}$ , with which  $\text{SnCl}_2$  forms a double salt not decomposable by  $\text{H}_2\text{O}$  or by exposure to air.

posed by acids, Au being left; it is unaffected by light; it is insoluble in the fixed alkalies, but soluble in  $\text{NH}_4\text{HO}$ , forming a deep purple solution from which it is deposited unchanged if the ammonia be expelled by heat or neutralized by an acid. The ammoniac solution is bleached by the action of light and Au is deposited. Purple of Cassius, when mixed with a little borax or some fusible glass, and applied to the surface of china, imparts to it a beautiful rose or a rich purple color. It is this compound which is added as the coloring material in the red glass of Bohemia."

226. *Hydrides of As and Sb.*—As and Sb form with H gaseous compounds, viz., arsenuretted hydrogen  $\text{AsH}_3$ , and antimonuretted hydrogen  $\text{SbH}_3$ ; these compounds may be prepared—1. By acting upon metallic arsenides and antimonides with acids:—\*



2. By the action of nascent hydrogen, evolved, for instance, from Zn and  $\text{H}_2\text{SO}_4$ , upon soluble arsenic and antimony compounds:—



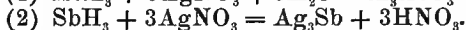
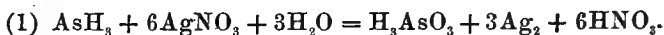
Fe and Sn act much less efficiently than Zn in producing these compounds. The  $\text{SbH}_3$  is always mixed with free H. The H evolved from the negative pole of a battery of several cells converts  $\text{As}_2\text{O}_3$  into  $\text{AsH}_3$ , but a weak current produces only a deposit of As; electrolytic H converts a portion only of the Sb of soluble antimony compounds into  $\text{SbH}_3$ , the remainder of the Sb being deposited in the metallic state on the negative plate.

227. The nascent H evolved by the action of KHO on Zn or Al, combines with As in arsenites forming  $\text{AsH}_3$ , but it does not act upon antimony compounds and form  $\text{SbH}_3$ ; hence Fleitman generates hydrogen in this manner to distinguish between As and Sb (par. 229).

228.  $\text{AsH}_3$  and  $\text{SbH}_3$  are colorless gases, the former has a most unpleasant odor, the latter is odorless; if passed through a heated tube they are decomposed into their elements, as they decompose below a red heat. When burnt

\* *Water* decomposes the compounds of the alkaline metals with As and Sb,  $\text{AsH}_3$  and  $\text{SbH}_3$  being formed along with the hydrate of the alkali.

in the air they yield  $\text{H}_2\text{O}$  and  $\text{As}_2\text{O}_3$ , and  $\text{Sb}_2\text{O}_3$ , respectively. If the supply of air is limited by depressing the *flame*, with a piece of porcelain for instance, the H only is oxidized, the metal, being set free, is deposited on the porcelain, if cold. They are decomposed by Cl and by  $\text{SO}_2$ ,  $\text{HNO}_3$ , aqua regia, and by all oxygenated acids, including strong  $\text{H}_2\text{SO}_4$ ; they are also decomposed by solutions of mercury, and most other heavy metallic salts. They are decomposed when passed through concentrated  $\text{HNO}_3$ ,  $\text{H}_3\text{AsO}_3$ , and  $\text{H}_3\text{AsO}_4$ , and  $\text{Sb}_2\text{O}_5$  being formed. When passed through a solution of  $\text{AgNO}_3$  the following changes ensue:



229. If a solution containing  $\text{H}_3\text{AsO}_3$ , or an arsenite, be mixed with a large excess of a concentrated solution of KHO, and boiled with fragments of granulated Zn,  $\text{H}_3\text{As}$  is evolved, and may be readily recognized by allowing it to pass on to a piece of filter-paper moistened with a solution of  $\text{AgNO}_3$ ; the paper assumes a purplish-black color, even when a small quantity of arsenic is present. This test serves to distinguish As from Sb (*Fleitmann*).

230. As forms one other compound with H; it is a brown powder, and is obtained by passing an electric current through water, the negative pole being formed of metallic arsenic. Its formula appears to be  $\text{AsH}_x$ .

#### GENERAL CHARACTERS OF THE SALTS OF THIS GROUP.

231. Stannous salts are either colorless or possess a yellowish tinge, they have a disagreeable metallic taste, and rapidly abstract oxygen from the air and from oxygen compounds, and become converted into stannic salts. When largely diluted with water their solutions become *milky*: on the addition of a small quantity of HCl they are again rendered clear. Stannic oxide forms two hydrates distinguished as stannic ( $\text{H}_2\text{SnO}_3$ ) and metastannic hydrates ( $\text{H}_2\text{Sn}_2\text{O}_{11}, 4\text{H}_2\text{O}$ ), the  $\text{H}_2\text{SnO}_3$  is obtained by adding  $\text{NH}_4\text{HO}$  to a solution of  $\text{SnCl}_4$ ; it is an amorphous gummy substance, soluble in HCl,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{T}$ , and in KHO and NaHO, but not in  $\text{NH}_4\text{HO}$ .  $\text{H}_2\text{Sn}_2\text{O}_{11}, 4\text{H}_2\text{O}$  is obtained by heating Sn or SnO with  $\text{HNO}_3$ , it is insoluble in  $\text{H}_2\text{T}$ , and in  $\text{HNO}_3$ ; when heated with concentrated  $\text{H}_2\text{SO}_4$ , it readily dissolves, forming a compound soluble in water,

but on boiling the solution the compound is decomposed, the two acids separating. It is also insoluble in  $\text{HCl}$ , but it forms with it a compound insoluble in acids, but soluble in water; it is readily soluble in solutions of the fixed alkalies and their carbonates, but it is not dissolved by  $\text{NH}_4\text{HO}$  unless recently precipitated from a cold solution of its salts by the addition of an acid. By a heat of  $284^\circ\text{C}$ . stannic is converted into a metastannic acid, and the latter is converted into the former by fusion with an excess of caustic alkali. Both these acids unite with bases and form salts; the metastannates can exist only in the hydrated state, and those of potash and soda are the only ones soluble in water; the soluble stannates have a strong alkaline reaction, and their solutions absorb  $\text{CO}_2$  from the air. Stannic hydrate dissolves in the stronger acids, forming stannic salts; these salts can also be prepared by adding to solutions of stannous ones an excess of acid, and then adding  $\text{Cl}$  or a small quantity of  $\text{HNO}_3$ . The stannic salts of the oxygen acids are very unstable. The acid properties of stannic hydrate are more powerful than the basic ones.  $\text{Na}_2\text{SO}_4$ ,  $\text{NH}_4\text{NO}_3$ , and most of the neutral salts of the alkalies, if added in excess, and the solution be not too acid, precipitate from both the stannates and metastannates their hydrates. Some of the antimonious salts are decomposed by ignition, the haloid salts volatilize readily and unaltered; the antimony salts are decomposed when treated with a large quantity of water into *soluble acid* and insoluble basic salts; the basic salts are distinguished from the basic bismuth salts formed under like circumstances by being dissolved by a solution of  $\text{H}_2\text{T}$ , in which the latter are insoluble. The hydrate  $\text{HSbO}_2^*$  possesses more of the characters of a base than of an acid, nevertheless it can combine with bases. Potassic antimonious tartrate (tartar emetic)  $\text{KSbC}_4\text{H}_4\text{O}_7$  is employed in medicine; it is prepared by boiling three parts of  $\text{Sb}_2\text{O}_3$  with four parts of  $\text{KHC}_4\text{H}_4\text{O}_6$  for about half an hour, renewing the water as it evaporates and filtering whilst hot; it is viewed by many chemists as containing the monatomic radical antimonyl ( $\text{SbO}$ ); its formula according to this view is  $\text{K}(\text{SbO})'\text{C}_4\text{H}_4\text{O}_6$ , and it is named potassic antimonylic tartrate. Arsenious acid unites with bases in several proportions; the arsenites are not very stable; the alkaline are the only arsenites soluble in  $\text{H}_2\text{O}$ , their concentrated

\* The normal hydrate  $\text{H}_3\text{SbO}_3$  is not known.

solutions are decomposed by the  $\text{CO}_2$  in the air; the insoluble arsenites are dissolved with decomposition by  $\text{HCl}$ . The arsenites of the metals of the alkalis and alkaline earths are decomposed by heat into arseniates,  $\text{As}$  being given off; plumbic arsenite is not decomposed by heat; the other arsenites are decomposed by heat,  $\text{As}_2\text{O}_3$  being given off, and the metal left as oxide unless it is reducible by heat. Potassic arsenite is used in medicine under the name of *Fowler's solution*, and  $\text{CuHAsO}_3$ , and the double salt of arsenite and acetate of copper ( $3\text{CuAs}_2\text{O}_3$ ,  $\text{Cu}_2\text{C}_2\text{H}_3\text{O}_2$ ) are employed as pigments, the first under the name of *Scheele's green* and the latter under the name of *Schweinfurt* or *emerald green*. Arsenic acid is a powerful acid, it takes away the bases from volatile acids; its salts have the general formula  $\text{M}'_3\text{AsO}_4$ ; one or two atoms of  $\text{M}'$  can be replaced by an equal number of atoms of  $\text{H}$ ; the alkaline arseniates are soluble in water, but the other arseniates are insoluble; most of the arseniates can bear a strong red heat without suffering decomposition. The salts of gold and platinum are decomposed on ignition.  $\text{KHO}$ ,  $\text{NaHO}$ ,  $\text{NH}_4\text{HO}$ , and their carbonates produce in solutions of stannous salts a precipitate of  $\text{SnH}_2\text{O}_2$ , and in solutions of stannic salts a precipitate of stannic or metastannic hydrate, according to the nature of the solution; these different precipitates are soluble in an excess of  $\text{KHO}$  or  $\text{NaHO}$ , but are insoluble in an excess of the other precipitants; these reagents precipitate also  $\text{Sb}_2\text{O}_3$  from solutions of  $\text{SbCl}_3$ , and also from other salts of  $\text{Sb}_2\text{O}_3$  but from solutions of tartar emetic less completely, and only after the lapse of some time; the precipitate redissolves pretty readily in  $\text{KHO}$  or  $\text{NaHO}$ , but requires the application of heat for its solution in  $\text{K}_2\text{CO}_3$ , and is altogether insoluble in  $\text{NH}_4\text{HO}$ . Zinc precipitates from stannous, stannic, and antimonious solutions in the presence of free  $\text{HCl}$ , the metal; if the reduction takes place in a platinum vessel the part of the platinum covered by the liquid is stained brown or black by  $\text{Sb}$  but not by  $\text{Sn}$ ;  $\text{HCl}$  does not remove the stain, hot  $\text{HNO}_3$  removes it immediately. The members of this group are distinguished from those of the other groups by the solubility of their sulphides in the alkalis and alkaline sulphides; unlike the members of the previous groups, but like those of the sixth, they are precipitated from their acid solutions by  $\text{H}_2\text{S}$ .

REMARKS ON THE INDIVIDUAL MEMBERS OF THE GROUP, WITH  
ADDITIONAL SPECIAL TESTS.

232. *Sn and its compounds.*—Sn has very little tenacity; it can easily be obtained in crystals; it is expanded by combined hammering and heating into sheets or leaves called *tin foil*.  $\text{SnO}_2$  occurs native as *tin stone* or *cassiterite*; this is the only ore of tin that is worked. Tin is a constituent of several important alloys. Speculum metal for the mirrors of reflecting telescopes, bell metal, and gun metal, are alloys of Sn and Cu; and the bronze used for coin consists of 95 pts. Cu, 4 of Sn, and 1 of Zn; solder is an alloy of Sn and Pb, and the amalgam of Sn and Hg is employed for the silvering of mirrors.

233.  $\text{AuCl}_3$  produces, in solutions of stannous salts containing a small quantity of free  $\text{HNO}_3$ , a precipitate (purple of Cassius).

234. If a solution of a stannous salt is added to a mixture of  $\text{K}_6\text{Fe}_2\text{Cy}_{12}$  and  $\text{Fe}_2\text{Cl}_6$ , Prussian blue precipitates immediately. This delicate test for a stannous salt can only be conclusive in cases where there are no other reducing agents present.

235. Solution of  $\text{HgCl}_2$  produces in solutions of stannous salts a white precipitate of  $\text{HgCl}$ , owing to the tin salt withdrawing half the Cl from the  $\text{HgCl}_2$ . If sufficient quantity of the tin salt be present, it removes, after a time, all the Cl from the Hg; the color of the precipitate then becomes gray. Since this reaction takes place even in highly dilute solutions, and in the presence of much free HCl, it is very valuable for the detection of stannous compounds.

236. If  $\text{Na}_2\text{CO}_3$  be mixed with equal parts of KCy and stannous or stannic compounds, and the mixed mass be subjected, upon a charcoal support, to the inner blowpipe flame, *ductile metallic grains of TIN* will be obtained, unaccompanied by any incrustation upon the charcoal.\*

237. *On the charcoal splinter* the Sn compounds are easily reduced to white, lustrous, ductile, metallic beads.

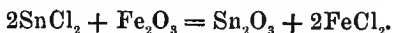
\* Bloxam has pointed out that if the KCy contains any  $\text{K}_2\text{SO}_4$ , the whole of the Sn is not obtained in the metallic state; if the quantity of  $\text{K}_2\text{SO}_4$  is small, a portion of the Sn is converted into  $\text{SnS}$ , which separates as a *black* powder on treating the fused mass with  $\text{H}_2\text{O}$ ; if there be much  $\text{K}_2\text{SO}_4$ , a portion of the Sn is converted into  $\text{SnS}_2$ , which is found in the aqueous solution of the fused mass, and from which it may be precipitated by HCl.

The flattened particles, transferred to the curved glass, slowly dissolve in  $\text{HCl}$ ; and the solution, when absorbed by paper, gives a red precipitate with selenious, and a black precipitate with tellurous acid dissolved in  $\text{HCl}$ . If to the solution a trace of bismuth-nitrate be added, an excess of soda gives a black precipitate of  $\text{Bi}_2\text{O}_3$ . The metal, acted on by  $\text{HNO}_3$ , yields a white powder of insoluble  $\text{SnO}_2$ .

238. *A borax bead*, containing enough  $\text{CuO}$  to render it faintly blue, serves as a delicate test to ascertain with certainty the presence of a trace of a  $\text{Sn}$  compound, as the bead, placed in the lower reducing flame, turns reddish-brown, or forms a clear ruby-red glass.—*Bunsen*.

239. Whether the  $\text{Sn}$  exists as a stannous or a stannic compound may be ascertained by adding to one portion of the solution  $\text{HgCl}_2$ ,  $\text{AuCl}_3$ , or a mixture of  $\text{K}_6\text{Fe}_2\text{Cy}_{12}$  and  $\text{Fe}_2\text{Cl}_6$ , and by adding another portion to a hot concentrated solution of  $\text{Na}_2\text{SO}_4$ . These, along with the blowpipe tests, are characteristic of  $\text{Sn}$ .

240. Another oxide,  $\text{Sn}_2\text{O}_3$ , is known. It is obtained as a slimy gray hydrate by boiling  $\text{Fe}_2\text{H}_6\text{O}_6$  in a solution of  $\text{SnCl}_2$ :—



It dissolves in  $\text{NH}_4\text{HO}$ , which distinguishes it from  $\text{SnO}$ ; and it is distinguished from  $\text{SnO}_2$  by forming with  $\text{AuCl}_3$  a purple precipitate. It does not appear to form definite salts.

241. *Sb and its compounds*.— $\text{Sb}$  is a brilliant bluish-white metal. It is hard, and so brittle that it can be easily reduced to powder. It is inferior to most of the metals as a conductor of heat and electricity. In the state of fine powder it is easily dissolved by digesting it in a solution of a potassic polysulphide. If one part of tartar emetic is dissolved in four parts of a solution of  $\text{SbCl}_3$ , and the solution is subjected to the action of two or three cells of Smee's battery, using a plate of  $\text{Sb}$  for the positive, and a copper wire for the negative electrode, a metallic deposit of  $\text{Sb}$ , having the color and lustre of highly-polished steel, and a bright metallic amorphous fracture, is deposited, the deposit retains 5 or 6 per cent. of  $\text{SbCl}_3$ . This amorphous  $\text{Sb}$ , when heated or struck, undergoes a rapid and intense molecular change throughout its mass, attended with great evolution of heat, increasing, at the same time, in density; it retains its cohesion and metallic aspect, but becomes



gray, and acquires a granular fracture, and an increased density. The change is attended with an abundant disengagement of fumes of  $\text{SbCl}_3$  (*Gore*). Sb is a constituent of several important alloys. It confers on these compounds hardness and the property of expansion in the act of solidification. Ordinary type metal is composed of 3 or 4 parts of Pb and 1 of Sb; the best is composed of 2 parts of Pb, 1 of Sn, and 1 of Sb. The principal mineral of Sb is the sulphide  $\text{Sb}_2\text{S}_3$ .

242. Introduce an antimonial solution into the apparatus (fig. 2), and add some Zn and dilute  $\text{H}_2\text{SO}_4$ , the presence of Sb in the evolved gas may be recognized by the following reactions:—

1st. The gas will burn with a *bluish-green flame*, emitting white fumes of *teroxide of antimony*, which may be condensed in a cold beaker, dissolved in *hydrochloric acid* and tested with *hydrosulphuric acid*.

2d. If the inner surface of a porcelain capsule be depressed upon the flame, a *black spot* of metallic antimony will be deposited upon it, which is lustrous, only when in thin layers. This deposit is distinguished from the similar arsenical stain by its solubility in solution of chloride of soda ( $\text{NaClO}$ ), and by its ready solubility in  $(\text{NH}_4)_2\text{S}$ . Another method of testing the deposit is to moisten it with  $\text{HNO}_3$  of sp. gr. 1.42, then heat the vessel over a lamp, and blow over the surface to cause the acid to evaporate; the white deposit which remains will turn deep black with ammonio-nitrate of silver.

3d. The glass tube from which the gas issues should be heated with a spirit lamp, in the centre; a *lustrous mirror of antimony* will be deposited on the inside of the tube, immediately around the flame of the lamp, whilst the bluish-green tint of the hydrogen flame in great measure disappears. The means for distinguishing this mirror from the arsenical one are given at pars. 262—2d, and 263.

243. These reactions should be compared with those of terhydride of arsenic under similar circumstances.

244. If a solution of  $\text{Sb}_2\text{O}_3$  in one of the fixed alkalies is mixed with a solution of  $\text{AgNO}_3$ , a deep black precipitate of  $\text{Ag}_4\text{O}$  forms with the grayish-brown precipitate of  $\text{Ag}_2\text{O}$ . Upon now adding  $\text{NH}_4\text{HO}$  in excess, the  $\text{Ag}_2\text{O}$  is redissolved, whilst the  $\text{Ag}_4\text{O}$  is not (*H. Rose*). This very delicate test enables one to detect readily the presence of  $\text{Sb}_2\text{O}_3$  in the presence of  $\text{Sb}_2\text{O}_5$ .

245. *Detection of Sb in organic mixtures.*—If it be in

the solid state it should be cut up into small pieces ; if it is a liquid, and in large quantity, it should by evaporation be reduced to a convenient bulk. It is then mixed with HCl and  $\text{KClO}_3$ , as directed at par. 733 ; from the filtered liquid the Sb may be precipitated by  $\text{H}_2\text{S}$ , or it may be introduced into the apparatus (fig. 2) and the gas tested for Sb, as directed in par. 242—1st, 2d, and 3d.

246. If compounds of Sb, mixed with  $\text{Na}_2\text{CO}_3$  and KCy, be exposed, upon a charcoal support, to the reducing flame of the blowpipe, brittle grains of Sb will be formed, accompanied with a *white* incrustation on the charcoal.

247. *Flame coloration*, by treatment in the upper reducing flame, pale green, unaccompanied by any smell.

248. *Reduction film*, black, sometimes dead, sometimes bright.

249. *Oxide film*, white ; moistened with a perfectly neutral solution of  $\text{AgNO}_3$ , and then blown on by ammoniacal air, it gives a black spot which does not disappear in  $\text{NH}_4\text{HO}$ . If the film be first placed over bromine vapor the reaction cannot be obtained, owing to the oxidation of  $\text{Sb}_2\text{O}_3$  into  $\text{Sb}_2\text{O}_5$ . It is unaltered by  $\text{SnCl}_2$ , either with or without  $\text{NaHO}$ .

250. *Iodide film*, orange red, disappearing by breathing, and reappearing by blowing or warming ; blown on with ammoniacal air it disappears, but does not return. Generally it gives the same reactions as the oxide.

251. *Sulphide film*, orange red. The film is difficult to blow away with  $\text{NH}_4\text{S}_2$  ; returns on blowing with air ; insoluble in water.

252. *With soda on charcoal splinter* gives no black stain on silver, but yields a white, brittle, metallic bead.

*Characteristic reactions*.—The orange-colored precipitate with  $\text{H}_2\text{S}$ , the *film reactions*, and the decomposition of the neutral salts by water, and the solubility of the precipitate in  $\text{H}_2\text{T}$ .

253. Two other oxides of Sb are known, viz.  $\text{Sb}_2\text{O}_4$ , which is generally regarded as composed of equal equivalents of  $\text{Sb}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_5$ , and is therefore named antimoniate of antimony. This oxide is obtained by heating strongly  $\text{Sb}_2\text{O}_5$ , which loses by the ignition one-fifth of its O and becomes converted into  $\text{Sb}_2\text{O}_4$ , or it may be obtained by roasting  $\text{Sb}_2\text{O}_3$  in the air. It is white, infusible, and unalterable by heat ; slightly soluble in  $\text{H}_2\text{O}$ , more soluble in HCl ; it is resolved into  $\text{Sb}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_5$  on boiling it in a solution of  $\text{KHT}$ . The other oxide is  $\text{Sb}_2\text{O}_6$ , it is called antimonic

oxide, or anhydride, and is obtained by heating below redness one of its hydrates. It is a yellowish powder insoluble in water and acids, but soluble in a solution of  $\text{KHO}$ ; and when fused with  $\text{K}_2\text{CO}_3$  the  $\text{CO}_2$  is expelled, and potassic antimoniate is left. It appears to form three hydrates, forming three distinct acids, thus:  $\text{H}_3\text{SbO}_4$ , the normal hydrate;  $\text{HSbO}_3$ , antimonie acid;  $\text{H}_4\text{Sb}_2\text{O}_7$ , metantimonie acid.

254. *As and its compounds*.—As has a brilliant dark steel-gray lustre. It is very brittle, and is easily reduced to powder.  $\text{As}_2\text{O}_3$  is the arsenic, or *white arsenic*, of the shops. There are two varieties of this oxide, one, from its appearance, is termed the vitreous, and the other the milky variety; when heated, they volatilize in white inodorous fumes. Both kinds are more easily soluble in hot than in cold water.  $\text{As}_2\text{O}_2$  is exceedingly poisonous; and being altogether inodorous, almost destitute of taste, and readily obtainable, is frequently employed as a poison. The best antidote is the moist and well-washed ferric hydrate. *Arsenic anhydride* ( $\text{As}_2\text{O}_5$ ) is a white solid; it has no action on litmus paper; is nearly insoluble in  $\text{H}_2\text{O}$  and in  $\text{NH}_4\text{HO}$ ; it fuses at a low red heat without undergoing decomposition, but at a higher temperature it is resolved into  $\text{O}$  and  $\text{As}_2\text{O}_3$ , which volatilizes. *Arsenic acid* ( $\text{H}_3\text{AsO}_4$ ) is readily soluble in water, and it may be obtained in large transparent crystals by exposing a concentrated solution to a very low temperature. Its aqueous solution dissolves  $\text{Zn}$  and  $\text{Fe}$  with evolution of  $\text{H}$ ; but if  $\text{H}_2\text{SO}_4$ , or  $\text{HCl}$ , is present it is reduced and converted into  $\text{H}_3\text{As}$ .  $\text{SO}_2$  passed through a solution of it reduces it to  $\text{As}_2\text{O}_3$ ,  $\text{H}_2\text{SO}_4$  being formed. The greater part of  $\text{As}_2\text{O}_3$  of commerce is prepared from mispickel ( $\text{FeAsS}$ ), an arsenical sulphide of iron furnished abundantly by the Silesian mines; and from the arsenides of  $\text{Ni}$  and  $\text{Co}$ , which yield  $\text{As}_2\text{O}_3$ , as a secondary product in the ordinary process of working these ores. In the manufacture of shot a small quantity of  $\text{As}$  is added to the  $\text{Pb}$  to facilitate its assuming the globular form.

#### BEHAVIOR OF $\text{As}_2\text{O}_3$ AND THE ARSENITES WITH REAGENTS.

255.  $\text{AgNO}_3$  produces in neutral solutions of the arsenites a yellow precipitate of  $\text{Ag}_3\text{HASO}_3$ , soluble in  $\text{HNO}_3$  and  $\text{NH}_4\text{HO}$ ;  $\text{AgNO}_3$ , therefore, produces no precipitate, or only a slight turbidity in solutions of  $\text{As}_2\text{O}_3$ , but on

neutralizing the acid with  $\text{NH}_4\text{HO}$  the precipitate appears. Ammonio-nitrate of silver is, therefore, a more appropriate reagent than  $\text{AgNO}_3$  if the acid be free.

256.  $\text{CuSO}_4$  produces in neutral solutions of the arsenites a yellowish-green precipitate of  $\text{CuHAsO}_3$  soluble in  $\text{NH}_4\text{HO}$ , and in acids;  $\text{CuSO}_4$  produces, therefore, no precipitate in solutions of  $\text{As}_2\text{O}_3$  but on neutralizing the acid with  $\text{NH}_4\text{HO}$  the precipitate appears; ammonio-sulphate of copper is, therefore, a more suitable reagent than  $\text{CuSO}_4$  in testing an acid solution.

257. If to a solution of  $\text{As}_2\text{O}_3$ , or an arsenite, solution of  $\text{KHO}$  be added in excess, and a few drops only of a *dilute* solution of  $\text{CuSO}_4$ , and the liquid subsequently boiled, a red precipitate of  $\text{Cu}_2\text{O}$  will fall down, whilst the solution will contain POTASSIC ARSENIATE. This test is particularly applicable in distinguishing  $\text{As}_2\text{O}_3$  from  $\text{As}_2\text{O}_5$ . It cannot be employed with safety as a direct means for detecting  $\text{As}_2\text{O}_3$ , as many organic substances possess the property of reducing  $\text{CuO}$  to the state of  $\text{Cu}_2\text{O}$ .

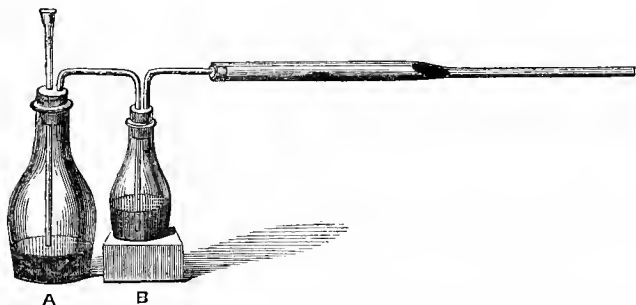
258. "If to  $\text{As}_2\text{O}_3$ , no matter whether in the solid form or in solution, some  $\text{HC}_2\text{H}_3\text{O}_2$  is added, and then  $\text{KHO}$  in slight excess, the mixture evaporated to dryness, and the residue heated to redness in a small tube—or if a trace of  $\text{As}_2\text{O}_3$  is introduced into a narrow test-tube, and there covered with a somewhat larger quantity of  $\text{NaC}_2\text{H}_3\text{O}_2$ , and heat applied—part of the  $\text{As}_2\text{O}_3$  is reduced, but there forms at the same time ALKARSIN (oxide of cacodyl)  $2(\text{As}(\text{CH}_3)_2)\text{O}$ , which makes its presence immediately known by its equally characteristic and formidable odor, which somewhat resembles that of sharp onions. This changes speedily to the not less characteristic odor of chloride of cacodyl ( $\text{As}(\text{CH}_3)_2\text{Cl}$ ), if the ignited contents of the tube are heated with a few drops of  $\text{SnCl}_4$ ."—*Bunsen*.

259. If arsenites, or  $\text{As}_3\text{O}_3$ , or  $\text{As}_2\text{S}_3$ , are fused together with a mixture of equal parts of dry  $\text{Na}_2\text{CO}_3$  and  $\text{KCy}$ , the whole of the  $\text{As}$ , and also the base, if an easily reducible one, is reduced to the metallic state, the  $\text{O}$  converts part of the  $\text{KCy}$  into  $\text{KCyO}$ . In the reduction of  $\text{As}_2\text{S}_3$ ,  $\text{KCyS}$  is formed. The operation is conducted as follows: Introduce the perfectly dry arsenic compound into the bulb of a small bulb-tube, and cover it with six times the quantity of a perfectly dry mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{KCy}$ . The whole quantity must not more than half fill the bulb, otherwise the fusing  $\text{KCy}$  is likely to ascend into the tube. Apply the heat of a lamp to the bulb, and continue this

for a while, as the As frequently requires some time for its complete sublimation. The metallic mirror is deposited on the cold part of the tube of exceeding purity; and is obtained from all arsenites whose bases remain either altogether untouched, or are reduced to arsenides which lose their As partly or totally upon the application of heat. By this method minute quantities of As can be detected, and it is especially adapted for obtaining As from  $\text{As}_2\text{S}_3$ . The delicacy is increased by heating the mixture in a stream of dry  $\text{CO}_2$ , as described in the next par.

260. The apparatus (fig. 1) consists of a flask A capable of holding about eight or twelve fluidounces; it is fitted with a funnel-tube, and a bent tube which dips into a smaller flask, B. In A  $\text{CO}_2$  is slowly generated from

Fig. 1.



pretty large fragments of marble (no powder) and dilute  $\text{HCl}$ ; it is conveyed into B, which is partly filled with concentrated  $\text{H}_2\text{SO}_4$ , in order to dry the gas. The exit-tube from B is bent at right angles, and connected, by means of a cork, with the reduction-tube; this latter tube is made out of a piece of hard glass tube (combustion-tube) somewhat more than three-eighths of an inch in diameter, and drawn out at one extremity to a long point; the length of the body of the tube should be about four inches, that of the point at least two and a half inches.

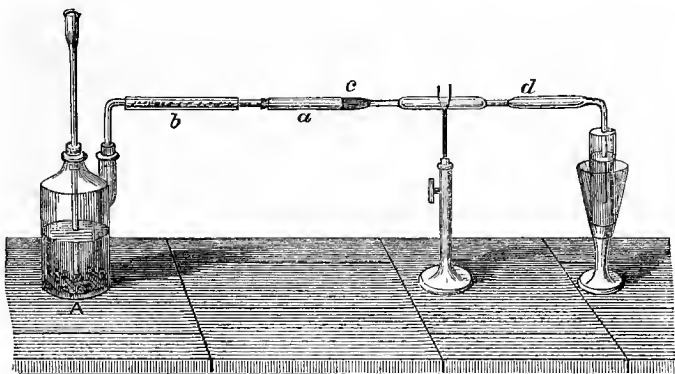
261. A mixture of 3 parts of anhydrous  $\text{Na}_2\text{CO}_3$  and 1 part of  $\text{KCy}$  is dried in the water bath; about 12 parts of this dried mixture is mixed with 1 part of  $\text{As}_2\text{S}_3$ , or the arsenite, which has been also dried in the water-bath; the mixture, before it has time to get damp, is put upon a narrow slip of card-paper bent into the shape of a gutter;

it is then introduced into the tube, and the latter is turned half round upon its axis; the mixture falls upon the glass, and the gutter is withdrawn. The mixture should be in the middle of the tube, and it ought not to occupy more than an inch. The reduction-tube must now be fixed, by means of the cork, to the exit-tube of B, and a moderate stream of  $\text{CO}_2$  ought to be evolved, by pouring some  $\text{HCl}$  into A, by means of the funnel-tube. Heat the reduction-tube, in its whole length, very gently with a lamp, until the mixture is perfectly dry; when all the water is expelled, moderate the gas stream so that only one bubble shall pass through the  $\text{H}_2\text{SO}_4$  in B in a second; the gas stream may be moderated by pouring water into A. When the gas stream is moderated, apply the flame of a lamp to the shoulder of the tube; and when this part of the tube is red hot, apply the flame of a second lamp, commencing at the end of the reduction-tube nearest B, and heating along up to the mixture; continue to apply the flame at the part where the mixture is, until all the As is expelled. The far greater portion of the volatilized As recondenses in the narrow part of the tube, whilst an extremely minute portion only escapes through the fine point, imparting to the surrounding air the peculiar odor of garlic. Advance the flame of the second lamp slowly and gradually up to the first, by which means the whole of the As which may have condensed in the wide part of the tube is driven into the narrow part. When this end has been attained, close the fine point of the tube by fusion, and apply heat, proceeding from the closed point towards the part where the greater part of it is condensed, by which means the extent of the mirror is narrowed, whilst its beauty and lustre are correspondingly increased. In this manner, perfectly distinct mirrors of As may be produced from as little as the one-hundredth part of a grain of  $\text{As}_2\text{S}_3$ . No mirrors are obtained by this process from  $\text{Sb}_2\text{S}_3$ , nor from any other compound of Sb.

262. *Marsh's test for Arsenic.*—The apparatus (fig. 2) is a convenient one, as the  $\text{AsH}_3$  can be both tested by reagents, decomposed in the tube by heating the tube, and the  $\text{AsH}_3$  may also be burnt as it escapes from the opening of the tube, and the As deposited in the tube and the  $\text{As}_2\text{O}_3$  produced by burning the gas can each be tested. A is a flask for the acid, the Zn, and the solution to be tested. It is provided with a funnel-tube for conveying the liquids. b is a tube filled with fragments of fused calcic chloride for

drying the gas.  $cd$  is a tube of hard-glass (free from lead) about one-quarter of an inch in diameter, and having, as shown in the figure, two or three capillary contractions, and bent at a right angle, so that it may form a jet, or that it may dip into a solution of  $\text{AgNO}_3$ .

Fig. 2.



The first thing to be ascertained is whether the Zn and dilute  $\text{H}_2\text{SO}_4$  to be employed are free from As; for this purpose they must first be introduced into A, *without* the solution to be tested, and after the evolution of the H has continued long enough to expel all the air, the tube is to be heated at  $a$  for about five or ten minutes, and the escaping gas conducted into a solution of  $\text{AgNO}_3$ . If no deposit is produced in the tube or a precipitate in the Ag solution, the Zn and  $\text{H}_2\text{SO}_4$  are free from As, and the solution to be examined for As may be introduced into A,\* and the evolved gas then examined in the following manner:—

1st. Hold a piece of filter-paper, moistened with a solution of  $\text{AgNO}_3$ , over the open end of  $cd$ ; if  $\text{H}_3\text{As}$  is present the paper will assume a *purplish-black* color. In flame the gas, if  $\text{H}_3\text{As}$  is present it will burn with a *livid blue* flame, producing a white smoke of  $\text{As}_2\text{O}_3$ ; condense the  $\text{As}_2\text{O}_3$  by holding a wide, cold test-tube over the flame; dissolve the condensed matter in hot water, and test it for  $\text{H}_3\text{AsO}_3$ , especially with ammonio-nitrate of silver, and with  $\text{H}_2\text{S}$ , after acidifying with  $\text{HCl}$ .

\* If there is much frothing when organic matter is present, a little alcohol must be added to prevent it.

2d. Heat the tube at *a* by means of a lamp, As will be deposited a little beyond the flame as a steel-gray ring; after a sufficient deposit has been obtained at that point, remove the lamp to the next division and obtain a second deposit; if necessary, a third may be obtained in the third division. Let the escaping gas during the heating of the tube pass into a solution of  $\text{AgNO}_3$ ; when the operation is over the portions of the reduction-tube containing the deposits may be cut off with a file and the deposits examined. The As deposit is soluble in a solution of chloride of soda ( $\text{NaClO}$ ), and it is perceptibly dissolved if a drop of  $(\text{NH}_4)_2\text{S}$  be added to it. If the crust be dissolved in concentrated  $\text{HNO}_3$ , and evaporated just to dryness upon a sand-bath, a little water added, and afterwards ammonio-nitrate of silver, a *brick-red precipitate* of  $\text{Ag}_3\text{AsO}_4$  will be obtained; an antimony spot, when treated in this way, generally gives a slight dirty white precipitate with the Ag solution. The  $\text{AgNO}_3$  solution, through which the gas has been passed, ought to be examined for As as in the fifth method (par. 218).

263. Another method for distinguishing which of the two metals, As or Sb, has produced the mirror, and also for distinguishing and detecting the two metals when they occur together, is the following: Having obtained the mirror in the tube *cd* in the manner already described (par. 262—2d), a feeble stream of dry  $\text{H}_2\text{S}$  must be transmitted through the tube, the metallic mirrors being gently heated from their outward to their inward border. If only As be present, the yellow sulphide  $\text{As}_2\text{S}_3$  will be formed. If Sb only be present, the orange or black  $\text{Sb}_2\text{S}_3$  will be produced; but if both metals be present, the two sulphides will be formed; and the  $\text{As}_2\text{S}_3$ , being the more volatile of the two, will be the further removed from the flame. A stream of dry  $\text{HCl}$  gas must be passed through the tube without the application of heat; by this means the  $\text{Sb}_2\text{S}_3$  will be converted into volatile  $\text{SbCl}_3$ , which will entirely disappear, whilst the  $\text{As}_2\text{S}_3$  will remain unaltered, and may be distinguished from any sulphur which may have separated, by dissolving readily in  $\text{NH}_4\text{HO}$ .

264. In employing Marsh's test for the detection of As it is necessary, as has already been stated, to have the solution free from  $\text{Cl}$ ,  $\text{HNO}_3$ ,  $\text{HClO}_3$ ,  $\text{SO}_2$ , aqua regia, mercury salts, etc.  $\text{SO}_2$  may be present if the organic matter has been carbonized by  $\text{H}_2\text{SO}_4$  and the presence of  $\text{SO}_2$  may give rise to the production of  $\text{H}_2\text{S}$  by the action of



the nascent H upon it;  $H_2S$  may also be formed if the  $H_2SO_4$  is not sufficiently diluted to prevent its acting too violently upon the Zn.  $H_2S$  must not be present, because it would form with the arsenic  $As_2S_3$ , which is not converted by the H into  $AsH_3$ . In conclusion, it may be remarked that the presence of organic matter sometimes completely prevents the detection of minute quantities of As by Marsh's method.

265. If clean metallic copper is boiled in a solution containing  $As_2O_3$ , acidified with HCl, the copper becomes coated with a *steel-gray film* of As; if the quantity of  $As_2O_3$  is considerable, the reduced As will separate from the Cu, when the liquid is boiled for some time, in *large black scales*. As many other metallic oxides are reduced to their metallic state under the same circumstances, it is necessary to submit the crust to further examination. This test, which is called "Reinsch's test," is particularly useful for the detection of As in organic liquids or solids. "The suspected liquid is simply to be acidulated with about one-sixth of its bulk of HCl, and boiled. The solid tissue must be cut up into very small pieces, and boiled for some time in a mixture of about one part of HCl with six of water, until the whole is disintegrated; then strained through muslin, or filtered through a previously wetted filtering paper.

266. "Into either of the above boiling liquids dip the end of a piece of clean polished copper wire; examine the wire from time to time, and as soon as its surface acquires a gray metallic discoloration remove it, and add in its stead fragments of fine copper gauze, continuing the supply as long as the last added piece assumes any definite alteration in color.

267. "Remove the pieces of copper gauze, wash them in water, and dry them between folds of filtering paper; the deposit will not rub off unless the amount of As be very large. If the As exist in but very small quantity, the color of the precipitated metal is bluish; otherwise of a dark iron-gray tint. Holding the piece of gauze in the fingers, warm it over a flame, coil it up into a small compass, and introduce it into a reduction-tube: now apply heat cautiously; the As will volatilize, oxidize, and condense in the cold part, in the form of a white crystalline sublimate. Several pieces of coated gauze may be thus treated successively, until a sufficiently obvious sublimate of  $As_2O_3$  is procured; by examination with a lens, or with

the low power of a microscope, the crystals will be seen to consist of highly iridescent octo- and tetra-hedra." File off the piece of tube containing the sublimate, boil it for a minute or two in a little water; test the water after the boiling for  $\text{As}_2\text{O}_3$ , one portion with  $\text{HCl}$  and  $\text{H}_2\text{S}$ , and another portion with ammonio-nitrate of silver.

268. As is not deposited on the Cu in the presence of oxidizing bodies, and the  $\text{HCl}$  in their presence dissolves the Cu. When present they must be got rid of by reduction or other means before introducing the copper foil or gauze. As a small quantity of Cu is always dissolved, the foil or gauze employed should be at least so far free from As that a solution of four or five grains of it should not yield a perceptible trace of it. The  $\text{HCl}$  to be employed should also be free from As; its purity may be conveniently ascertained by diluting it with three or four times its own volume of water and boiling in it, for some time, a piece of the copper foil to be employed; if pure, the Cu will not be stained. We may observe, in conclusion, that the arsenical film which peels off from the Cu is not pure As, but an arsenide of copper ( $\text{Cu}_3\text{As}_2$ ). On heating the copper foil in the tube only a portion of the As, and relatively only a small portion, volatilizes, the rest of it remains behind united with the Cu.

269. *Detection of As in organic mixtures.*—Before examining for arsenic in articles of food and dead bodies, it is necessary in the generality of cases to destroy the organic matter before attempting to search for the arsenic compound, as, from its consistence, etc., it impedes the application of the reagents or masks their reactions; the destruction involves the use of chemical reagents, which as far as possible ought to be avoided, on account of the difficulty of obtaining many of them perfectly free from arsenic; as by the *dialytic* method no chemical reagent of any kind is introduced into the organic mixture, it is desirable first to dialyse the suspected organic matter; for this purpose the solid portion is cut into small pieces, the mixed solid and liquid portion is then placed in the dialyser\* to the depth of not more than half an inch, the dialyser is then floated in a basin containing a volume of water about four times greater than the organic fluid. After twenty-four hours about three-fourths of the  $\text{As}_2\text{O}_3$

\* The dialyser ought to be about ten inches in diameter, and perfectly sound. See the Author's "Second Step in Chemistry," p. 681.

(or other crystalloid poison) will be found in the water of the basin, which is generally colorless. To this liquid, after concentration on the water-bath, all the ordinary tests of arsenic may be applied.

270. *Destruction of the organic matter.*—Sulphuric acid, hydrochloric acid and potassic chlorate, chlorine, aqua regia, nitric acid and potassic nitric, sulphuric acid and sodic chloride, have been respectively proposed and recommended by different chemists for the destruction of the organic matter in the examination for arsenic in medico-legal cases; we shall describe a few of these methods.

1st. The organic matter, after it has been minutely divided, is mixed with about a fifth of its weight of *pure* concentrated  $\text{H}_2\text{SO}_4$ , and heated for some time, continually stirring with a glass rod; the mass becomes brown and finally black, and white fumes of  $\text{H}_2\text{SO}_4$  are evolved along with  $\text{SO}_2$ ; the heat must be continued, but not so high as to volatilize any arsenic, until the residue is reduced to a *dry friable* carbonaceous mass; it is then pulverized, and afterwards treated with a small quantity of concentrated  $\text{HNO}_3$  for oxidizing  $\text{As}_2\text{S}_3$ , which may have been contained in the suspected matter, or which may have been formed by the simultaneous reduction of  $\text{H}_2\text{SO}_4$  and the  $\text{As}_2\text{O}_3$  during the carbonization; the mixture is again evaporated to dryness to expel completely the  $\text{HNO}_3$ ; it is then boiled in water and filtered, and the filtrate examined for arsenic by Marsh's test. The employment of  $\text{H}_2\text{SO}_4$  was proposed by MM. Flandin and Danger. The process is open to some objections; some  $\text{NaCl}$  will always be present in the organic matter, and under certain conditions  $\text{AsCl}_3$  will be formed by the reciprocal reaction of the  $\text{H}_2\text{SO}_4$ , the  $\text{NaCl}$  and the  $\text{As}_2\text{O}_3$ ; the  $\text{AsCl}_3$ , if formed, will volatilize, and consequently escape detection;\* it is also very difficult to obtain  $\text{H}_2\text{SO}_4$  perfectly free from arsenic.

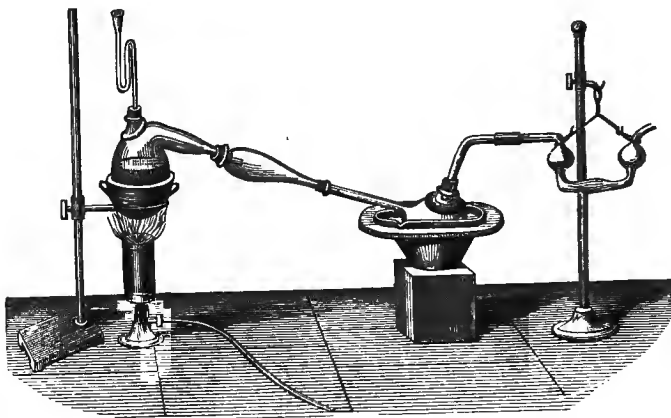
2d. The employment of  $\text{HCl}$  and  $\text{KClO}_3$  for the destruction of the organic matter possesses many advantages; it is certain, and in the examination other metallic poisons as well as arsenic can be sought for and detected, and it allows of a quantitative determination of the poison; the process is described in par. 733.

3d. M. Schneider has proposed to separate the arsenic

\* To avoid this loss it has been proposed to conduct the operation in a retort, and collect any matter that distils over in water, but this modification renders the method less simple and convenient.

from the organic matter with which it is mixed by converting it into the volatile  $\text{AsCl}_3$ ; for this purpose the organic mixture under examination is introduced into a retort (fig. 3) and a quantity of  $\text{NaCl}$  added, and then

Fig. 3.



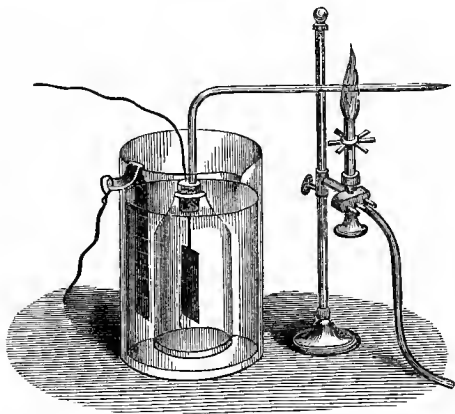
through the safety tube a little at a time some pure concentrated  $\text{H}_2\text{SO}_4$ ; the mixture is then distilled, the receiver being kept cool; the three-bulb tube connected with it contains distilled water. It is necessary to keep the  $\text{NaCl}$  in the retort in excess, to prevent the formation of  $\text{SO}_2$ , when the liquid becomes concentrated in the retort. As  $\text{AsCl}_3$  is decomposed by  $\text{H}_2\text{O}$ , it cannot be formed when there is much of that liquid present; if the organic mixture contains much water it ought, therefore, to be concentrated by distilling it by the aid of the water-bath before adding the  $\text{NaCl}$  and  $\text{H}_2\text{SO}_4$ . The distillate is diluted with water and treated with  $\text{H}_2\text{S}$ , and the  $\text{As}_2\text{S}_3$  is reduced by  $\text{KCy}$  (259), or it is converted into  $\text{As}_2\text{O}_3$  by means of  $\text{HNO}_3$ ; the excess of the latter being expelled, the  $\text{As}$  is detected by means of Marsh's method.

271. Bloxam has proposed to employ the electric current for the conversion of  $\text{As}$  into  $\text{H}_3\text{As}$ . This, the electrolytic method of eliminating arsenic, possesses certain advantages over that of Marsh: 1. It avoids the use of  $\text{Zn}$ , and thereby obviates a frequent source of error arising from the presence of  $\text{As}$  in that metal. 2. It introduces no sub-

stances into the liquid that can interfere with its subsequent examination for other metals. If any other metals are present it precipitates them on the surface of the negative plate. When the  $\text{AsH}_3$  is obtained by means of  $\text{Zn}$ ,  $\text{Sb}$ , if also present, is evolved together with the  $\text{As}$ , and the subsequent separation of these two metals is troublesome; but with the electrolytic method only a very small quantity of  $\text{Sb}$  is evolved as  $\text{SbH}_3$ , and even this quantity may be completely arrested by adding to the liquid a solution of  $\text{H}_2\text{S}$ . Both  $\text{Sb}$  and  $\text{As}$  are then converted into sulphides, but the  $\text{As}_2\text{S}_3$  is converted by the electrolytic hydrogen as easily as  $\text{As}_2\text{O}_3$  into  $\text{AsH}_3$ , whereas the  $\text{Sb}_2\text{S}_3$  completely resists the action of it, and consequently remains in the liquid.

272. The apparatus consists of a two-ounce narrow-mouthed bottle, the bottom of which has been cut off and replaced by a piece of vegetable parchment, tightly stretched over it and secured by a ligature of thin platinum wire (a ligature of organic matter is quickly destroyed). The bottle is furnished with a cork, in which is fitted air-tight

Fig. 4.



a quill tube bent at right angles; also a platinum wire, to which is attached a plate of the same metal, which forms the negative pole of the voltaic circuit; it is also convenient to have fitted in the cork, although it is not shown in fig. 4, a funnel tube for introducing the liquid to be tested.

The bottle is placed within a glass of such a size as to leave a small interval between the two, and this glass is allowed to stand in a vessel of cold water. About an ounce of dilute  $\text{H}_2\text{SO}_4$  is introduced into the apparatus, so as to fill the bottle and the outer vessel to about the same level, the positive plate being immersed in the acid in the outer vessel. The current of a voltaic battery (six Grove's cells of ordinary size) is then passed through the arrangement, and when the bottle has become filled with hydrogen the tube is heated to redness during fifteen minutes, to ascertain the purity of the  $\text{H}_2\text{SO}_4$ ; the liquid to be tested is then introduced into the bottle by means of the funnel tube, or by a pipette, the cork being removed for an instant; a drachm of alcohol is also added to prevent frothing; the heating of the reduction-tube is then continued for thirty minutes before the absence of arsenic is inferred.

273. The following method has been recommended by Bloxam for the detection of poisonous metals by electrolysis, viz: The mixture, which may, of course, have been previously examined for organic poisons by the usual methods, is digested on a water-bath, with so much water,  $\text{HCl}$ , and  $\text{KClO}_3$  as may be required to disintegrate the solid organic portions, and to render the liquid capable of filtration; the filtrate is evaporated on the water-bath to a small bulk; it is then treated with an excess of  $\text{H}_2\text{S}$  water, and introduced into the decomposing cell along with some alcohol, to prevent frothing; and the passage of the current is continued for about an hour. In the heated tube the  $\text{As}$ , if present, will be found, and on the negative plate and in the liquid the other poisonous metals will have to be sought for. 1st. As regards the tube, the  $\text{As}$ , if  $\text{H}_2\text{S}$  or  $\text{SO}_2$  has been introduced into the decomposing cells, is deposited either in part or entirely as  $\text{As}_2\text{S}_3$  in the tube a little beyond the heated portion; there is generally a deposit also of  $\text{As}$ , and if an excess of  $\text{H}_2\text{S}$  has been employed a deposit of  $\text{S}$ , which is nearer the orifice than the deposit of  $\text{As}_2\text{S}_3$ , and from which it may easily be distinguished by its much lighter color, and by its insolubility in a warm solution of  $\text{NH}_4\text{HCO}_3$ , which readily dissolves  $\text{As}_2\text{S}_3$ . It is probable that the deposit of  $\text{As}_2\text{S}_3$  is occasioned by the  $\text{AsH}_3$  and  $\text{H}_2\text{S}$  reacting upon each other under the influence of heat. If  $\text{H}_2\text{S}$  is added, and no  $\text{As}$  is present, a thin white film of  $\text{S}$  will generally be deposited in the tube. 2d. If no  $\text{H}_2\text{S}$  has been em-

ployed, the metals to be sought for on the negative plate are Sb, Hg, Cu, and Bi; the plate having been washed, is boiled in somewhat dilute yellow  $(\text{NH}_4)_2\text{S}$  for a minute or two. This solution is then evaporated on a watch-glass placed in the water-bath, and the orange residue of  $\text{Sb}_2\text{S}_3$  identified by the usual tests. The platinum plate having been again washed is boiled in a few drops of concentrated  $\text{HNO}_3$ , to which a drop of dilute  $\text{HCl}$  should be added to dissolve the  $\text{HgS}$ . The acid solution is boiled down to a small bulk and mixed with an excess of  $\text{NH}_4\text{HO}$ , by which the presence of Cu will be rendered evident, and the  $\text{Bi}_2\text{O}_3$  will be precipitated, together with a little  $2\text{NH}_4\text{Cl}$ ,  $\text{PtCl}_4$ . To examine for Bi the precipitate is dissolved in  $\text{HCl}$  evaporated and largely diluted with  $\text{H}_2\text{O}$ . The filtered ammoniacal liquid, acidulated with  $\text{HCl}$ , and boiled with clean copper, will prove the presence or absence of Hg. If  $\text{H}_2\text{S}$  has been added, this plan will have to be modified, as the  $\text{Sb}_2\text{S}_3$  and other sulphides which have been formed will be found suspended in the liquid of the decomposing cell, and not deposited in the metalline state on the negative plate.

274. *Flame reactions*.—1. *Flame-coloration* in upper reducing flame pale blue, giving the well-known arsenical smell.

2. *Reduction-film* black, dead or brilliant, thin film brown.

3. *Oxide-film* white; touched with a perfectly neutral solution of  $\text{AgNO}_3$ , and then blown with ammoniacal air, it gives a canary-yellow precipitate, soluble in  $\text{NH}_4\text{HO}$ . Together with this yellow precipitate, a brick-red one of silver-arsenate occurs when the film has previously been treated with bromine vapor.  $\text{SnCl}_2$ , with and without soda, produces no change.

4. *Iodide-film* is deep yellow, disappears on breathing, but returns on drying; disappears in ammoniacal air, and does not return; reappears unaltered after the action of  $\text{HCl}$ .

5. *Sulphide-film* lemon yellow, disappears easily on blowing with  $(\text{NH}_4)_2\text{S}$ , and reappears on warming or blowing; insoluble in  $\text{H}_2\text{O}$ , and does not disappear by breathing.

6. *Reduction on charcoal splinter* yields no metallic bead.

BEHAVIOR OF ARSENIC ACID AND THE ARSENIATES  
WITH REAGENTS.

275.  $\text{AgNO}_3$  produces, in neutral solutions of the arseniates, a characteristic reddish-brown precipitate of  $\text{Ag}_3\text{AsO}_4$ , soluble in dilute  $\text{HNO}_3$  and in  $\text{NH}_4\text{HO}$ ;  $\text{AgNO}_3$  produces, therefore, no precipitate, or only a slight turbidity in solutions of  $\text{H}_3\text{AsO}_4$ , but on neutralizing the acid with  $\text{NH}_4\text{HO}$  the precipitate appears; ammonio-nitrate of silver is, therefore, a more appropriate reagent than  $\text{AgNO}_3$  if the acid be free.

276.  $\text{CuSO}_4$  produces, in neutral solutions of the arseniates, a greenish-blue precipitate of  $\text{CuHAsO}_4$ .

277.  $\text{MgSO}_4$ , in the presence of  $\text{NH}_4\text{Cl}$  and of  $\text{NH}_4\text{HO}$ , produces, in solutions of the arseniates, a white precipitate of  $\text{MgNH}_4\text{AsO}_4$ , soluble in acids.

278.  $\text{H}_3\text{AsO}_4$  produces, not only with magnesian salts, but also with ferric salts and with ammonic molybdate, precipitates similar in appearance and in constitution to those produced by these reagents with  $\text{H}_3\text{PO}_4$ , but it is distinguished from this latter acid by the color of its silver salts, and by its conversion into  $\text{As}_2\text{S}_3$  on being treated with  $\text{H}_2\text{S}$ .

279. Nascent  $\text{H}$ , evolved by the action of  $\text{Zn}$  on dilute  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$ , converts  $\text{H}_3\text{AsO}_4$ , as it does  $\text{As}_2\text{O}_3$ , into  $\text{H}_3\text{As}$ , but the conversion is much slower, and in those reactions which depend upon the reduction to the metallic state  $\text{H}_3\text{AsO}_4$  resembles  $\text{As}_2\text{O}_3$ .

280. Whether  $\text{As}$  exists as  $\text{As}_2\text{O}_3$  or as  $\text{H}_3\text{AsO}_4$  may be ascertained by testing a portion of the original solution with the copper test (257), and another portion of the original solution with the silver (275) or magnesian test (277).

281. *Au and its compounds.*— $\text{Au}$  is the only metal of a yellow color. It unites with nearly all the metals, but its most important alloys are those which it forms with  $\text{Ag}$  and  $\text{Cu}$ . The standard gold for coin in England contains 8.33 per cent. of  $\text{Cu}$ . In France and the United States it contains 10 per cent. of  $\text{Cu}$ . Jewellers frequently alloy their gold with  $\text{Ag}$  as well as  $\text{Cu}$ ; the  $\text{Ag}$  gives it a lighter color. The solder used for gold trinkets is composed of 5 parts of  $\text{Au}$  and 1 part of  $\text{Cu}$ , or of 4 parts of  $\text{Au}$ , 1 part of  $\text{Cu}$ , and 1 part of  $\text{Ag}$ . Gold is always found in the metallic state generally more or less alloyed with  $\text{Ag}$ .



282. Ferrous salts precipitate Au from its solutions as a *bluish-black* precipitate, which acquires a metallic lustre when rubbed.

283. A solution of  $\text{SnCl}_2$  and some  $\text{SnCl}_4$  produces, even in very dilute solutions of Au, a purple precipitate (purple of Cassius), the tint of which varies according to the quantity of Au present. The precipitate is insoluble in *dilute acids*; the Au solution should be first mixed with the  $\text{SnCl}_4$ , and the  $\text{SnCl}_2$  then added drop by drop. When the quantity of Au is extremely minute, a *pink tinge* pervades the solution.

284. A very delicate method of applying this test is as follows:  $\text{Fe}_2\text{Cl}_6$  is added to  $\text{SnCl}_2$  until a permanent yellow color is produced; the solution is then considerably diluted; the Au solution, having likewise been much diluted, is poured into a beaker, which is placed on a sheet of white paper; a glass rod is dipped into the Fe solution, and afterwards into the Au solution, when, if even a trace of Au be present, a *blue or purple streak* will be observed in the track of the glass rod. This test has the advantage of being applicable even in very acid solutions.

285. One other oxide of gold is known, viz. the aurous oxide  $\text{Au}_2\text{O}$ . It is a green powder, and is obtained by decomposing  $\text{AuCl}_3$  with a cold solution of KHO.

286. *Pt and its compounds.*—Pt in compact masses is white, but in a finely divided state, obtained by precipitation, it is as black as soot, and is termed *platinum black*. It is obtained as a gray, porous, slightly coherent mass, called spongy platinum, by igniting the double chloride of  $2\text{NH}_4\text{Cl}$ ,  $\text{PtCl}_4$ . Pt possesses the valuable property of uniting when two masses of it are pressed or hammered together at a high temperature. This operation of uniting masses of metal into one is termed "welding." Wollaston, who first devised a process of working Pt, made use of this property. He purified the Pt from other metals by boiling it in  $\text{HNO}_3$ . He then dissolved it in aqua regia, and converted it into  $2\text{NH}_4\text{Cl}$ ,  $\text{PtCl}_4$ . From this salt he obtained "spongy platinum." This was heated, compressed, and hammered, until it became homogeneous and ductile, and had a sp. gr. of about 21.5. Deville and Debray have lately proposed a new plan. They dissolve out the Pt from its ore by liquid Pb, which does not dissolve the impurities. The Pb is subsequently separated from the Pt by cupellation, and the Pt is finally melted in a crucible of lime by means of the oxyhydrogen blowpipe.

"The most important applications of Pt are confined to the laboratory of the manufacturing and experimental chemist; they depend upon its great infusibility and its power of resisting chemical reagents. Pt always occurs in the metallic state, usually in small flattened grains, in which it is mixed with palladium, rhodium, osmium, ruthenium, and iridium—metals which are rarely found except when associated with Pt."

287. KCl or  $\text{NH}_4\text{Cl}$  produces, in solutions of Pt, a yellow crystalline precipitate of  $2\text{KCl}$ ,  $\text{PtCl}_4$ , or  $2\text{NH}_4\text{Cl}$ ,  $\text{PtCl}_4$ . The presence of HCl promotes the formation of this precipitate. Dilute solutions should be evaporated along with the KCl or  $\text{NH}_4\text{Cl}$  and the HCl on the water-bath to dryness, and the residue digested in weak spirits of wine until the excess of the alkaline chloride employed is dissolved.

288. Solutions of platinic salts produce, in solutions of  $\text{SnCl}_2$ , which contain much HCl, a dark *brownish-red color*; in exceedingly dilute solutions the color is *yellow*, and becomes darker on standing. This test is a very delicate one for Pt. The dark brown color is owing to the reduction of the platinic to a platinous salt.

289. Platinum forms with oxygen another oxide, viz. platinous oxide ( $\text{PtO}$ ).

290. Answers to the following exercises must be written out:—

#### EXERCISES.

92. Give the results of the action of  $\text{Fe}''\text{SO}_4$  and of  $\text{H}_2\text{O}$  on  $\text{AuCl}_3$ .

93. Give the theory of the method of Marsh for the detection of As.

94. How would you distinguish the product of the action of  $\text{H}_2\text{O}$  on  $\text{SbCl}_3$  from the similar one produced on  $\text{BiCl}_3$  by  $\text{H}_2\text{O}$ ?

95. Describe by equations the reactions which take place when  $\text{H}_2\text{S}$  is passed into a solution of arsenious acid, through one of arsenic acid, and through one of tartar emetic.

96. Describe by equations the reactions which take place when a stannous salt is added to a mixture of  $\text{K}_6\text{Fe}_6\text{Cy}_{12}$  and  $\text{Fe}_2\text{Cl}_6$ , and to a solution of  $\text{HgCl}_2$ .

97. For what purposes is Pt employed in the metallic state, and how is it obtained in mass?

98. Describe the method proposed by Schneider for separating As from organic matters.

99. For what purposes is Sb employed in the arts in the metallic state?

100. Describe by an equation the reaction which takes place when a mixture of  $\text{As}_2\text{O}_3$ , KHO, and acetate acid is evaporated to dryness, and the residue heated, and what is the name of the arsenic compound which is produced.

101. Describe the dialytic method of separating crystalloid poisons from the contents of the stomach.

102. I have got some copper nickel,  $\text{NiAs}$ , containing some  $\text{CoAs}_2$ , and I wish to prepare some pure nickel: how shall I proceed?

103. Give an account of the method of employing electrolysis for the separation of As and Sb from liquids containing organic matter.

104. Give the composition of tartar emetic, a method for preparing it, its properties, and the action of chemical reagents upon it.

105. How would you convert arsenious acid into arsenic acid, and reconvert the latter acid into the former one; and how would you distinguish solutions of these acids from each other?

106. Describe the changes which take place when  $\text{As}_2\text{S}_3$  is digested with  $\text{H}_2\text{SO}_3$  and  $\text{KHSO}_3$ .

107. Describe by an equation the changes which take place when  $\text{H}_3\text{As}$  and  $\text{H}_3\text{Sb}$  are passed through a solution of  $\text{AgNO}_3$ .

108. What is the action of reagents upon argentic and cupric arsenite, and how would you detect the metals including As in these compounds?

109. Describe by an equation the changes which take place when a solution of an arsenious compound, KHO, and fragments of Zn are boiled together.

110. How do you account for the presence of As in HCl?

111. How are gun-barrels bronzed?

112. How would you detect and how remove the oxides of nitrogen and  $\text{As}_2\text{O}_3$ , so often present as impurities in sulphuric acid?

113. To what acid is the term aqua regia applied? and describe its chemical properties.

## SIXTH GROUP.

ARGENTIC OXIDE ( $\text{Ag}_2\text{O}$ ), MERCUROUS OXIDE ( $\text{Hg}_2\text{O}$ ), MERCURIC OXIDE ( $\text{HgO}$ ), BISMUTHOUS OXIDE ( $\text{Bi}_2\text{O}_3$ ), PLUMBIC OXIDE ( $\text{PbO}$ ), CUPRIC OXIDE ( $\text{CuO}$ ), CADMIC OXIDE ( $\text{CdO}$ ).

*For the reactions.*— $\text{AgNO}_3$ ,  $\text{HgNO}_3$ ,  $\text{HgCl}_2$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{CuSO}_4$ ,  $\text{CdCl}_2$  or  $\text{CdSO}_4$ ,—dissolved in  $\text{H}_2\text{O}$ ;  $\text{BiCl}_3$ , dissolved in dilute  $\text{HCl}$ .

291. The insolubility of  $\text{AgCl}$ ,  $\text{HgCl}_2$ , the slight solubility of  $\text{PbCl}_2$ , and the ready solubility of the other chlorides, enables one to divide this group into two sections.

*First section.*—The oxides which form with  $\text{HCl}$  insoluble chlorides are the members of this section. They are  $\text{Ag}_2\text{O}$ ,  $\text{Hg}_2\text{O}$ , and  $\text{PbO}$ .

*Second section.*—The oxides which do not form with  $\text{HCl}$  insoluble chlorides are the members of this section. They are  $\text{HgO}$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{CuO}$ ,  $\text{CdO}$ , and  $\text{PbO}$ , as the slight solubility of  $\text{PbCl}_2$  in water renders it impossible to confine this member exclusively to the first section—a portion of the  $\text{PbCl}_2$ , varying according to the amount of liquid present, always remaining dissolved; the  $\text{Pb}$  it contains is precipitated along with the members of the second section on the addition of  $\text{H}_2\text{S}$ . If attention be paid to the following facts, they will frequently remove a source of much confusion: 1. If  $\text{Pb}$  has been discovered in the first section, a precipitate must always be obtained on passing  $\text{H}_2\text{S}$  through the filtrate, even if no other member of the group be present. 2. If only a small quantity of  $\text{Pb}$  be present,  $\text{HCl}$  may cause no precipitate, as a sufficient quantity of water may be present to dissolve the chloride formed. In this case all the  $\text{Pb}$  will be found in testing for the members of the second section.

292. *Examination for the members of the first section.*—When a solution is examined for the members of this group only, the general reagent for this section must be added, as directed at par. 355; and when a precipitate is produced, it must be washed as there directed, and then examined according to the method described in next par.

293. Add boiling-water to the precipitate;  $\text{PbCl}_2$  will be dissolved, if present, which is ascertained by  $\text{H}_2\text{SO}_4$ , producing in the filtrate a precipitate of  $\text{PbSO}_4$ . If a residue remain after removing the  $\text{PbCl}_2$  by adding successively to the mixed chlorides fresh quantities of boiling water, until

the last washings give on the addition of  $\text{H}_2\text{SO}_4$  no further precipitate, it proves that either  $\text{AgCl}$  or  $\text{HgCl}$ , or both, must be present.  $\text{NH}_4\text{HO}$  being added to the residue, dissolves the  $\text{AgCl}$ , whilst it converts  $\text{HgCl}$  into the *black* mercurous ammoniac compound. To detect the  $\text{AgCl}$  in the ammoniac solution,  $\text{HNO}_3$  must be added in excess, which, by neutralizing the solvent, causes the  $\text{AgCl}$ , if present, to be re-precipitated.

294. *Examination for the members of the second section.*—When a solution is examined for the members of this group only, the general reagent must be added as directed at pars. 357 and 358, and when a precipitate is produced it must be washed until the last washings contain no trace of  $\text{Cl}$ ;\* it must then be examined according to the next par.

295. The washed precipitate must be boiled in *dilute*  $\text{HNO}_3$ . If it all dissolves, with the exception of a light yellow mass of sulphur,  $\text{HgO}$  is absent; but if, after boiling for some time, the undissolved mass presents a black appearance, it points out the probable presence of that member. Examine the black mass for  $\text{HgO}$ , as directed in par. 296. To the acid solution, after it has been filtered from the yellow or black mass, and subsequently evaporated nearly to dryness, so as to remove the greater part of the free acid, must be added a little water, and then a few drops of *dilute*  $\text{H}_2\text{SO}_4$ , which will precipitate the  $\text{Pb}$  as  $\text{PbSO}_4$  after the lapse of a longer or shorter time; the solution must therefore be allowed to stand some time before  $\text{NH}_4\text{HO}$  is added.  $\text{NH}_4\text{HO}$  being added in excess to the filtrate, throws down the  $\text{Bi}$  (confirm its presence according to par 324). The filtrate from the ammoniac precipitate, or the solution with which that reagent has failed to give a precipitate, is divided into two parts, which we shall call A and B.

A. The A portion is acidulated with acetic acid and tested for  $\text{Cu}$ , if the presence of that metal has not been already manifested by the blue color of the ammoniac solution, by adding to it  $\text{K}_4\text{FeCy}_6$ ; if *Cu is present*, a brownish-red colored precipitate will be produced; if *Cu is absent*, the color of the solution will not be altered by the reagent (346).

\* The removal of the  $\text{Cl}$  is ascertained by the wash-water giving no precipitate on the addition of a few drops of a solution of  $\text{AgNO}_3$ ; the wash-water to be tested must not be collected with the previous washings, but by itself, and in a *clean* test-tube.

TABLE VI.  
BEHAVIOR OF THE MEMBERS OF THE FIRST SECTION WITH THE SPECIAL REAGENTS.

(PbO.)	(Ag <sub>2</sub> O.)	(Hg <sub>2</sub> O.)
P 1. PbCl <sub>2</sub> is difficultly soluble in <i>cold water</i> ; it is much more soluble in <i>boiling water</i> . It is precipitated by H <sub>2</sub> SO <sub>4</sub> from its aqueous solutions as PbSO <sub>4</sub> , which is insoluble.	Q 1. AgCl is insoluble in <i>water</i> .	R 1. HgCl is insoluble in <i>water</i> .
P 2. PbCl <sub>2</sub> is very slightly soluble in NH <sub>4</sub> HO; the ammoniac solution becomes turbid after a short time, from the separation of the lead as an insoluble oxychloride (PbCl <sub>2</sub> · 3PbO, + H <sub>2</sub> O), which is soluble in HNO <sub>3</sub> ; it is therefore easily distinguished from AgCl.	Q 2. AgCl is easily soluble in NH <sub>4</sub> HO. On the addition of any acid in excess it is again precipitated from this solution.	R 2. HgCl does not dissolve in NH <sub>4</sub> HO, but becomes altered in color, the <i>white chloride</i> being converted into a <i>black compound</i> , di-mercurous ammonio chloride (Hg <sub>2</sub> H <sub>2</sub> NCl).

BEHAVIOR OF THE MEMBERS OF THE SECOND SECTION WITH THE SPECIAL REAGENTS.

(HgO.)	(PbO.)	(Bi <sub>2</sub> O <sub>3</sub> .)	(CdO.)	(CuO.)
S 1. HgS is <i>black</i> ; it is <i>insoluble</i> in <i>boiling HNO<sub>3</sub></i> , but is easily soluble in <i>squa regia</i> .	T 1. PbS is <i>black</i> ; it is <i>soluble</i> in <i>boiling HNO<sub>3</sub></i> .	U 1. Bi <sub>2</sub> S <sub>3</sub> is <i>black</i> ; it is <i>soluble</i> in <i>boiling HNO<sub>3</sub></i> .	V 1. CdS is <i>yellow</i> ; it is <i>soluble</i> in <i>boiling HNO<sub>3</sub></i> .	W 1. CuS is <i>black</i> ; it is <i>soluble</i> in <i>boiling HNO<sub>3</sub></i> .

S 2. $\text{HgSO}_4$ is decomposed, in the presence of much water, into an insoluble basic and a soluble acid salt.	T 2. $\text{H}_2\text{SO}_4$ precipitates, from solutions of lead, $\text{PbSO}_4$ , which is <i>insoluble</i> in water and dilute acids, freely soluble in ammoniac acetate and tartrate.	U 2. $\text{H}_2\text{SO}_4$ produces no precipitate in solutions of this oxide, $\text{Bi}_2(\text{SO}_4)_3$ being <i>soluble</i> in water.	V 2. $\text{H}_2\text{SO}_4$ produces no precipitate in solutions of this oxide, $\text{CdSO}_4$ being <i>soluble</i> in water.	W 2. $\text{H}_2\text{SO}_4$ produces no precipitate in solutions of this oxide, $\text{CuSO}_4$ being <i>soluble</i> in water.
S 3. $\text{NH}_4\text{HO}^*$ produces, in solutions of $\text{HgCl}_2$ , a WHITE PRECIPITATE ( $\text{Hg}_2\text{H}_4\text{N}_2\text{Cl}_2$ ), <i>insoluble</i> in an excess of the reagent.	T 3. $\text{NH}_4\text{HO}$ throws down, from solutions of plumbic salts, white basic salts, which are <i>insoluble</i> in an excess of the reagent.	U 3. $\text{NH}_4\text{HO}$ throws down, from solutions of $\text{Bi}$ , the HYDRATE, <i>insoluble</i> in an excess of the reagent.	V 3. $\text{NH}_4\text{HO}$ precipitates, from solutions of $\text{Cd}$ , $\text{CdH}_2\text{O}_2$ , <i>soluble</i> in an excess of the reagent.	W 3. $\text{NH}_4\text{HO}$ produces, in solutions of this oxide, a GREENISH BLUE precipitate, which <i>dissolves</i> with a beautiful azure color in an excess of the reagent.
S 4. $(\text{NH}_4)_2\text{CO}_3^\dagger$ behaves in the same way, in solutions of $\text{Hg}''$ , as of $\text{NH}_4\text{HO}$ .	T 4. $(\text{NH}_4)_2\text{CO}_3$ precipitates, from solutions of $\text{Pb}$ , $\text{PbCO}_3$ , <i>insoluble</i> in an excess of the reagent.	U 4. $(\text{NH}_4)_2\text{CO}_3$ throws down, from solutions of $\text{Bi}$ , a WHITE BASIC CARBONATE, <i>insoluble</i> in an excess of the reagent.	V 4. $(\text{NH}_4)_2\text{CO}_3$ throws down, from solutions of $\text{Cd}$ , $\text{CdCO}_3$ , <i>insoluble</i> in an excess of the reagent.	W 4. $(\text{NH}_4)_2\text{CO}_3$ behaves in the same way in solutions of $\text{Cu}$ as $\text{NH}_4\text{HO}$ .

\* The fixed alkalis precipitate all the members of this group from their solutions; the lead precipitate is difficultly soluble in an excess of the reagents; all the rest are insoluble. The precipitate produced by the fixed alkalies, in solutions of the  $\text{Hg}''$ , is the yellow oxide, unless ammoniac salts are present; in that case the precipitate is the same as that produced by  $\text{NH}_4\text{HO}$ .

† The fixed alkaline carbonates precipitate all the members of this group from their solutions. If added to cupric solutions in the cold, they produce a basic carbonate; but if the solution is boiled, it is converted into  $\text{CuO}$ .

B. The B portion, when Cu is absent, is examined for Cd in the following manner:  $(\text{NH}_4)_2\text{S}$  is added to the ammoniac fluid, and if it produces a *yellow precipitate* Cd is present.

When Cu is *present*, the B portion is examined for Cd in the following manner: Add a small quantity of dilute  $\text{H}_2\text{SO}_4$  to the solution and evaporate it to dryness and ignite, continuing the ignition until the ammoniac salt is expelled; then add a *concentrated* solution of  $\text{NH}_4\text{HCO}_3$ , and boil for a short time; *if no precipitate* is produced, Cd is absent. *If a precipitate is produced*, wash it with the  $\text{NH}_4\text{HCO}_3$  solution until all the Cu is removed; then dissolve the residue in a little dilute  $\text{HCl}$ , and afterwards add  $\text{NH}_4\text{HO}$  in excess, and finally *one drop* of  $(\text{NH}_4)_2\text{S}$ ; if a *yellowish precipitate\** is produced on the addition of the  $(\text{NH}_4)_2\text{S}$ , Cd is present.†

If Pb has not been discovered in either section, the black or light-colored precipitate insoluble in  $\text{HNO}_3$  ought to be digested in  $\text{NH}_4\text{A}$  and filtered, to the filtrate add  $\text{HA}$  in excess, and then a solution of  $\text{K}_2\text{CrO}_4$ ; if Pb is present, a yellow precipitate,  $\text{PbCrO}_4$ , will be formed.

296. If a black residue remain after boiling the mixed sulphides in  $\text{HNO}_3$ , it must be collected upon a filter, to separate it from the other members, and specially examined for  $\text{HgO}$  by one of the two following methods: 1st. After having dried the black mass thoroughly in a water-bath, mix it with dry  $\text{Na}_2\text{CO}_3$ , and proceed with the examination for Hg in the way described in par. 319. 2d. Dissolve the black mass in as *small a quantity* of AQUA REGIA as possible, or dissolve it by heating it with  $\text{HCl}$  and a few crystals of  $\text{KClO}_3$ , then add  $\text{NH}_4\text{HO}$  in slight excess, and then a slight excess of  $\text{HCl}$ ; examine the solution, thus prepared, for Hg by means of copper wire, in the way described at par. 314 or 315.

297. *The following precautions must be attended to in*

\* The reason for recommending the addition of only one drop of  $(\text{NH}_4)_2\text{S}$  is this—a small quantity of Cu frequently remains undissolved by the  $\text{NH}_4\text{HCO}_3$ ; in such case, if only a drop of  $(\text{NH}_4)_2\text{S}$  be added, the Cd, if present, will be first precipitated; whereas, if more  $(\text{NH}_4)_2\text{S}$  were added, the Cu would also be precipitated, and consequently obscure the Cd. When the color of the precipitate produced by  $(\text{NH}_4)_2\text{S}$  is black or of a doubtful color, it must, after being washed, be dissolved in  $\text{HNO}_3$ , the solution must be evaporated to dryness, and the residue treated as before with the concentrated solution of  $\text{NH}_4\text{HCO}_3$ , etc.

† For other methods for the separation of Cd and Cu, see par. 352.



*analyzing this group:* The means, both for separating and detecting the members of the first section are so simple and positive, that no difficulty will be experienced by the student. It may, nevertheless, be as well to observe, that  $\text{PbCl}_2$  ought to be completely removed before  $\text{NH}_4\text{HO}$  is added, for if it is not, a *white residue*, which is nothing more than  $\text{PbCl}_2$ , may remain after the addition of  $\text{NH}_4\text{HO}$ , when Hg is absent, which may perplex the student. And if the  $\text{PbCl}_2$  be not completely removed before the addition of  $\text{NH}_4\text{HO}$ , the ammoniac solution will appear turbid, owing to the separation of an insoluble basic salt of lead; this will not, however, interfere with the test for Ag, since it (the basic salt of lead) redissolves upon the addition of  $\text{HNO}_3$ . The difficulties which occur in examining the second section will be easily overcome by a little attention. Many erroneous conclusions will be formed if the simple yet necessary precaution of washing the  $\text{H}_2\text{S}$  precipitate be neglected, because a small quantity of the  $\text{HCl}$  employed to precipitate the first section, being left behind, will form with the  $\text{HNO}_3$  aqua regia, which, by dissolving the  $\text{HgS}$ , may cause that member to be overlooked; and should the mercury thus pass into solution, a compound of that metal will be precipitated on the addition of  $\text{NH}_4\text{HO}$ , which may be mistaken for Bi. The precipitate must, therefore, before it is treated with  $\text{HNO}_3$ , be washed with water until the wash-water, acidulated with  $\text{HNO}_3$ , gives no precipitate with  $\text{AgNO}_3$ . It is difficult to free the mass of sulphur, which separates on the addition of  $\text{HNO}_3$ , entirely from some of the undecomposed sulphides, which, by communicating to it a black appearance, might lead to the belief that  $\text{HgO}$  was present, even in the absence of that member. An experienced eye can generally distinguish between this mixture of undecomposed sulphide and sulphur, and  $\text{HgS}$ , the former being light and flocculent, whilst the latter is dense and heavy; but a safe and legitimate conclusion can only be arrived at by examining it specially for Hg. A varying amount of  $\text{H}_2\text{SO}_4$  is always formed by dissolving the sulphides in  $\text{HNO}_3$ : a portion of the Pb will therefore be precipitated as sulphate, and remain behind mixed with the substance insoluble in  $\text{HNO}_3$ ; it is necessary, on this account, to examine the insoluble mass for this member, if it should not be met with in its proper place. As  $\text{PbSO}_4$  precipitates from dilute solutions, and especially from those which contain much free acid, only after the lapse of some considerable time, the solution

ought, after the addition of  $\text{H}_2\text{SO}_4$ , to be allowed to stand for a considerable time (an hour) before adding the  $\text{NH}_4\text{HO}$ . A precipitate will be formed on the addition of  $\text{NH}_4\text{HO}$  to the solution in  $\text{HNO}_3$ , if either of these reagents contains a trace of Fe, but this precipitate cannot be mistaken for Bi if the confirmatory test be applied.

PROPERTIES OF THE METALS, THE OXIDES, THE SULPHIDES, THE CHLORIDES, THE NITRATES, THE SULPHATES OF THIS GROUP.

298. *The metals.*—None of the metals of this group, when perfectly pure, oxidize in *dry* air or oxygen at ordinary temperatures; in *moist* air or oxygen Pb, Bi, Cu, and Cd\* undergo a slight superficial oxidation; these four metals oxidize rapidly on exposure to air or oxygen at a *red heat*,  $\text{PbO}$ ,†  $\text{Bi}_2\text{O}_3$ ,  $\text{CuO}$ , and  $\text{CdO}$  being formed. Ag does not oxidize in air or O at any temperature; Hg oxidizes at  $371^\circ \text{C}$ .,  $\text{HgO}$  being formed; at  $427^\circ \text{C}$ . the oxide is decomposed into its elements. Ag, Hg, Pb do not decompose  $\text{H}_2\text{O}$ , even at a very elevated temperature; Bi and Cu decompose it at slightly elevated temperatures, and Cd decomposes it at a red heat. Cd is the only metal in this group which can displace the hydrogen in  $\text{H}_2\text{SO}_4$ ; the action takes place even when the acid is dilute,  $\text{CdSO}_4$  and  $\text{H}_2$  being formed; the dilute acid, and even the undiluted acid in the cold, has no action on the other metals,‡ but if they are boiled in the undiluted acid they become oxidized, sulphates of the metals,  $\text{H}_2\text{O}$  and  $\text{SO}_2$ , being formed.§  $\text{HCl}$  in solution has no action on Hg, and it only acts on Ag, Pb, Bi, and Cu when they are boiled in it, and even then very slowly;|| it acts readily on Cd,  $\text{CdCl}_2$  and  $\text{H}_2$  being formed.  $\text{HCl}$  in the gaseous state acts on Ag and Cu, when they are heated to redness in it, a chloride of the metal and  $\text{H}_2$  being formed.  $\text{HNO}_3$  oxidizes and dissolves

\* Pb, Bi, and Cd oxidize if exposed to the combined action of air and water.

† At a low red heat red lead ( $2\text{PbO}$ ,  $\text{PbO}_2$ ) is formed.

‡ If copper-foil be moistened with *dilute*  $\text{H}_2\text{SO}_4$  and then exposed to the air,  $\text{CuSO}_4$  will be formed.

§ A portion of  $\text{H}_2\text{SO}_4$ , in its action on Cu, suffers more complete decomposition, for sulphur is deposited.

||  $\text{HCl}$  with excess of air dissolves Cu at ordinary temperatures; the weaker acids, such as the acetic, have no effect upon Cu unless assisted by the oxygen of the air; the copper under such circumstances rapidly combines with O, and a salt of the acid is formed.

all the metals of this group, a nitrate of the metal being formed, and generally NO (nitric oxide) is the other nitrogen compound produced; but the degree of reducing action which these and other metals exercise on  $\text{HNO}_3$  varies with the *strength* of the acid and the *temperature*; for example, when Ag is acted upon by dilute  $\text{HNO}_2$  in excess at ordinary temperatures,  $\text{AgNO}_3$  and  $\text{HNO}_2$  (nitrous acid) and the anhydride are formed, but at higher temperatures the oxide of nitrogen formed is NO. When Cu and Hg are acted upon by  $\text{HNO}_3$  of moderate concentration, NO is disengaged, but with a stronger acid  $\text{N}_2\text{O}_4$  (nitric peroxide) is evolved, and if the action takes place at a higher temperature N is generally one of the gaseous substances set free.

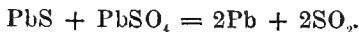
299. *The oxides.*— $\text{PbO}$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{CuO}$ , and  $\text{CdO}$ , may be formed either by exposing the metals to a red heat, in air or oxygen, or by igniting their hydrates, carbonates, or nitrates.  $\text{HgO}$  may be formed either by heating  $\text{Hg}(\text{NO}_3)_2$  or by heating Hg in air at a temperature of  $371^\circ \text{C}$ .  $\text{Ag}_2\text{O}$  and  $\text{Hg}_2\text{O}$  may be obtained by adding to a solution of any of their soluble salts a solution of KHO or NaHO, and drying the precipitate with care.  $\text{Ag}_2\text{O}$ ,  $\text{Hg}_2\text{O}$ , and  $\text{PbO}$  are perceptibly soluble in  $\text{H}_2\text{O}$ , the other oxides are not.  $\text{Ag}_2\text{O}$ ,  $\text{Hg}_2\text{O}$ , and  $\text{HgO}$  are decomposed by heat alone, the other oxides are not, they are, however, reduced to the metallic state on being heated in a current of H, or by being ignited in contact with C, and  $\text{PbO}$  and  $\text{Bi}_2\text{O}_3$  are reduced on being heated in an atmosphere of CO. The metals are obtained on fusing their oxides with KCy, potassic cyanate being formed. On being heated with an excess of S these oxides are converted into sulphides,  $\text{SO}_2$  being evolved. Dry Cl converts them into chlorides, the conversion in the case of  $\text{Ag}_2\text{O}$ ,  $\text{Hg}_2\text{O}$ , and  $\text{HgO}$  takes place without the aid of heat;  $\text{PbO}$ , suspended in  $\text{H}_2\text{O}$ , is converted by Cl into  $\text{PbO}_2$  and  $\text{PbCl}_2$ , a similar reaction takes place with Br. Some of the other oxides are converted by Cl in the presence of a solution of KHO into higher oxides. They all form hydrates with the exception of  $\text{Hg}_2\text{O}$ . The hydrate of argentine oxide, when dried at a temperature above  $60^\circ \text{C}$ ., is decomposed into  $\text{Ag}_2\text{O}$  and  $\text{H}_2\text{O}$ . The hydrates are formed by adding to the solution of these salts one of the alkalies in excess. The behavior of these oxides with the volatile and fixed alkalies is given in Table VI.  $\text{Ag}_2\text{O}$ ,  $\text{Hg}_2\text{O}$ , and  $\text{CuO}$  are black;  $\text{HgO}$  is black when hot, light red when cold;  $\text{Bi}_2\text{O}_3$  is yellow,  $\text{PbO}$

is also yellow or reddish-yellow;  $\text{CdO}$  is brown or yellowish-brown;  $\text{AgHO}$  is brown,  $\text{HgH}_2\text{O}_2$  is yellow,  $\text{CuH}_2\text{O}_2$  is light blue, and  $\text{PbH}_2\text{O}_2$ ,  $\text{CdH}_2\text{O}_2$ , and  $\text{Bi}_2\text{H}_6\text{O}_6$  are white.

300. *The sulphides.*—The sulphides of this group are insoluble in water, and dilute acids in the cold.  $\text{Ag}_2\text{S}$ ,  $\text{PbS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{CdS}$  are also insoluble in the alkalies, alkaline sulphides, and  $\text{KCy}$ ;  $\text{Hg}_2\text{S}$  and  $\text{HgS}$  are insoluble in solutions of the alkalies, ammoniac sulphide, and  $\text{KCy}$ , but these sulphides dissolve in  $\text{K}_2\text{S}$  or  $\text{Na}_2\text{S}$  in the presence of  $\text{NaHO}$  or  $\text{KHO}$ , the solution in the case of  $\text{Hg}_2\text{S}$  being attended with a separation of  $\text{Hg}$ .  $\text{CuS}$  is insoluble in the caustic alkalies, and in the fixed alkaline sulphides it dissolves only to a very trifling extent, but it is a little more soluble in ammoniac sulphide; it is soluble in a solution of  $\text{KCy}$ . They are all decomposed and dissolved with separation of sulphur in boiling  $\text{HNO}_3$ , with the exception of  $\text{Hg}_2\text{S}$  and  $\text{HgS}$ ; these latter, and also the other sulphides, are decomposed and dissolved by *aqua regia*. *Out of contact with the air*  $\text{Hg}_2\text{S}$  is decomposed at a gentle heat into  $\text{Hg}$  and  $\text{HgS}$ , which sublimes without fusing or decomposing;  $\text{Bi}_2\text{S}_3$  volatilizes at a red heat;  $\text{PbS}$  fuses at a red heat and volatilizes at a stronger heat without decomposing;  $\text{CuS}$  loses one-half its  $\text{S}$  on being heated, and becomes converted in  $\text{Cu}_2\text{S}$ , which is not decomposed by heat alone. If heated in a current of air or  $\text{O}$  they are decomposed,  $\text{Hg}$  and  $\text{Ag}$  being left in the metallic state, the other metals are left as oxides;  $\text{CuS}$  in the moist state oxidizes on exposure to the air at ordinary temperatures.  $\text{HgS}$ ,  $\text{Ag}_2\text{S}$ ,  $\text{PbS}$ ,  $\text{Bi}_2\text{S}_3$  are reduced to the metallic state on being heated strongly in a current of  $\text{H}$ ;  $\text{Cu}_2\text{S}$  is not reduced. Some of these sulphides, and probably all, undergo partial decomposition on being heated in a current of steam. On fusion with many metals, as  $\text{Fe}$ ,  $\text{Zn}$ ,  $\text{Cu}$ ,  $\text{Pb}$ ,  $\text{Sn}$ ,  $\text{Sb}$ , etc.,  $\text{HgS}$  and  $\text{Ag}_2\text{S}$  are decomposed, the added metal taking the  $\text{S}$ ;  $\text{PbS}$  is deprived of its  $\text{S}$  by  $\text{Fe}$ ,  $\text{Zn}$ ,  $\text{Cu}$ ,  $\text{Sn}$ , etc.;  $\text{Cu}_2\text{S}$  is not completely decomposed on fusing it with  $\text{Fe}$ ,  $\text{Sn}$ , or  $\text{Sb}$ . If  $\text{Cu}_2\text{S}^*$  or  $\text{Ag}_2\text{S}$  is roasted with  $\text{NaCl}$ ,  $\text{CuCl}$  or  $\text{AgCl}$  and  $\text{Na}_2\text{SO}_4$  are formed. If a solution of  $\text{CuCl}_2$  and  $\text{NaCl}$  is added to  $\text{Ag}_2\text{S}$ ,  $\text{AgCl}$  and  $\text{CuS}$  are formed.  $\text{PbO}$  and  $\text{CuO}$ , mixed with their sulphides in equivalent proportions and heated, yield the metals and  $\text{SO}_3$ ; and a mixture of their sulphates and sulphides in

\*  $\text{FeS}_2$  on being roasted with  $\text{NaCl}$  becomes converted into  $\text{Fe}_2\text{Cl}_6$ ,  $\text{Na}_2\text{SO}_4$  being formed.

equivalent proportions, on being heated, likewise yields the metal and  $\text{SO}_2$ , thus:—



The colors of the sulphides, *when obtained by precipitation*, are given in the table, with the exception of those of  $\text{Hg}_2\text{S}$  and  $\text{Ag}_2\text{S}$ , which are black. They can be obtained in the dry way by heating together the metal and S, with the exception of  $\text{Hg}_2\text{S}$  and  $\text{CuS}$ ; their color, *when so obtained*, is the same as that of the native sulphides; the *artificial* or *native*  $\text{Ag}_2\text{S}$  is *blackish gray*,  $\text{PbS}$  and  $\text{Bi}_2\text{S}_3$  are *lead gray*, the color of  $\text{CdS}$  is the same as that of the precipitated sulphide;  $\text{HgS}$  exists both amorphous and crystalline, the crystalline sulphide in mass is of a cochineal color and is called *cinnabar*, its powder is scarlet and is called *vermilion*; the amorphous sulphide is black, it is converted into the *red* both by sublimation and by the action of aqueous alkaline persulphides; the red is converted into the black by heating it moderately out of contact of the air.

301. *The chlorides.*— $\text{CuCl}_2$ ,  $\text{CdCl}_2$ , and  $\text{BiCl}_3$  may be obtained by dissolving their oxides or carbonates in  $\text{HCl}$ ;  $\text{HgCl}$  (calomel),  $\text{AgCl}$ , and  $\text{PbCl}_2$  are best formed by adding to any of their soluble salts in solution  $\text{HCl}$  or an alkaline chloride in solution;  $\text{HgCl}_2$  (corrosive sublimate) may be formed by dissolving  $\text{HgO}$  in boiling dilute  $\text{HCl}$ . In the dry way  $\text{HgCl}$  is formed by triturating equivalent proportions of  $\text{Hg}$  and  $\text{HgCl}_2$  until the metallic globules disappear, and then subliming the mixture.  $\text{HgCl}_2$  is formed by mixing intimately  $2\frac{1}{2}$  parts of  $\text{HgSO}_4$  and 1 part of  $\text{NaCl}$ , and then subliming the mixture, and  $\text{BiCl}_3$  may be formed by heating  $\text{Bi}$  in  $\text{Cl}$ , or by mixing  $\text{Bi}$  in fine powder with twice its weight of  $\text{HgCl}_2$  and then distilling.  $\text{HgCl}$  and  $\text{AgCl}$  are insoluble, but the latter is soluble in strong solutions of  $\text{NaCl}$ .  $\text{PbCl}_2$  is difficultly soluble, the other chlorides are soluble in water;  $\text{BiCl}_3$  is decomposed by  $\text{H}_2\text{O}$ ,  $\text{BiOCl}$  being formed, which is insoluble in  $\text{H}_2\text{O}$ , but soluble in diluted  $\text{HCl}$ . The chlorides of this group are not decomposed by heat alone; on being heated  $\text{HgCl}$  volatilizes below a red heat and without first melting;  $\text{HgCl}_2$ ,  $\text{BiCl}_3$ , and  $\text{CdCl}_2$  fuse before volatilizing; the first of these boils at  $295^\circ$ , the other two volatilize at a moderate heat;  $\text{AgCl}$  volatilizes partially at a red heat;  $\text{PbCl}_2$  not in contact with the air volatilizes at high temperatures, but in contact with air a portion volatilizes with excess of  $\text{Cl}$ , whilst a residue of  $\text{PbO}$ ,  $\text{PbCl}_2$  remains;  $\text{CuCl}_2$  at a

red heat loses half its Cl, CuCl remaining. They are all decomposed on being heated in a brisk current of hydrogen. They are all, with the exception of the mercury chlorides, decomposed when heated in a current of steam, the metal being left in the state of oxide, excepting in the case of bismuth and silver, the former of these being left as an oxychloride, the latter in the metallic state. With the exception of AgCl, HgCl, and HgCl<sub>2</sub>, they are all converted into oxides on being heated in a current of O or of atmospheric air.

302. *The nitrates.*—The oxides and their hydrates are readily soluble in HNO<sub>3</sub>, most of them form basic as well as neutral nitrates; the neutral nitrates are all soluble in water; Pb(NO<sub>3</sub>)<sub>2</sub> and Bi(NO<sub>3</sub>)<sub>3</sub> are, however, only sparingly soluble in H<sub>2</sub>O; HgNO<sub>3</sub>, Hg(NO<sub>3</sub>)<sub>2</sub>, Bi(NO<sub>3</sub>)<sub>3</sub> are decomposed by H<sub>2</sub>O, an insoluble, or sparingly soluble, salt being one of the substances formed. Freshly precipitated Ag<sub>2</sub>O decomposes Cu(NO<sub>3</sub>)<sub>2</sub> by boiling the oxide in a solution of that salt, CuO being precipitated, and AgNO<sub>3</sub> (lunar caustic) being formed.

303. *The sulphates.*—Bi<sub>2</sub>O<sub>3</sub>, CuO, CdO, and their hydrates dissolve readily in diluted H<sub>2</sub>SO<sub>4</sub>. HgSO<sub>4</sub> is decomposed by H<sub>2</sub>O into a sparingly soluble basic salt. PbSO<sub>4</sub> is insoluble in water, the sulphates of the other metals are soluble; Hg<sub>2</sub>SO<sub>4</sub> is decomposed by H<sub>2</sub>O, especially if hot, into a soluble acid and insoluble basic salt; under certain circumstances Bi<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> is decomposed by H<sub>2</sub>O into an insoluble salt. PbSO<sub>4</sub> is not decomposed by heat alone, the other sulphates are; but Ag<sub>2</sub>SO<sub>4</sub> is very difficultly reduced by heat, it is not decomposed by a red heat, bearing a much higher temperature than CuSO<sub>4</sub>, FeSO<sub>4</sub>, and Fe<sub>2</sub>SO<sub>4</sub>.

304. *The general characters of the salts of this group.*—The salts of Pb, Cd, and Bi are colorless if the acid be colorless; the soluble silver salts are colorless, so are many of the mercury salts, but some of the basic mercuric salts are yellow; many of the silver salts acquire a violet tint, and ultimately turn black on exposure to light; the cupric salts in the anhydrous state are white, but in the hydrous state they are blue or greenish-blue, which color their solutions exhibit even when much diluted. The soluble neutral silver salts are neutral, but the soluble neutral salts of the other metals of the group are acid, to test-paper. The mercurous and mercuric salts volatilize when heated either with or without decomposition; the soluble neutral salts of Ag, Bi, Cd, and Cu are decomposed at a

red heat; the plumbic salts sustain a red heat without alteration, unless the acid is very volatile or decomposable. The basic salts of Pb are alkaline to test-paper. Nearly all the silver salts are anhydrous. Ag and Hg are precipitated from the solutions of their soluble salts by many reducing agents, as  $\text{SO}_2$ ,  $\text{FeSO}_4$ , and by the following metals: Fe, Zn, As, Sb, Sn, Bi, Cu, Cd, Pb; and Hg also precipitates Ag. Fe, Zn, and other metals separate Ag from AgCl in the presence of  $\text{H}_2\text{O}$ . Hg, on being separated, frequently forms an amalgam with the metal; Bi is precipitated from its solutions by Zn, Fe, Sn, Cd, Pb, and Cu; Pb is thrown down by Zn, Cd, Sn, and slowly by Fe; Cu is precipitated by Zn, Fe, Cd, Sn, Pb; and Cd is precipitated from its solutions by Zn.  $\text{BaCO}_3$  or  $\text{CaCO}_3$  precipitates  $\text{CuO}$ ,  $\text{Hg}_2\text{O}$ ,  $\text{HgO}$ ,  $\text{Bi}_2\text{O}_3$ , as hydrates from solutions of their salts by digesting them in the solution.

REMARKS ON THE INDIVIDUAL MEMBERS OF THIS GROUP,  
WITH ADDITIONAL SPECIAL TESTS.

305. Ag and its compounds.—Ag is the whitest of all metals; in the finely divided state, as obtained by the precipitation of metals, it is a dull dark gray powder. It is harder than Au, and softer than Cu. It melts at a white heat. Its conductivity for electricity and heat is greater than that of any other metal; its conductivity decreases with the temperature. It combines with Cl, Br, I, at ordinary temperatures, and readily with S, P, and As. It undergoes no change when heated in contact with melted alkaline nitrates or with the hydrates of the alkalis; crucibles of silver are, therefore, very useful when these substances have to be fused, as Pt is acted upon by them in their fused state. The affinity of  $\text{Ag}_2\text{O}$  for acids is greater than that of  $\text{CuO}$  and  $\text{ZnO}$ .  $\text{Ag}_2\text{O}$  is insoluble in the fixed alkalis, but readily soluble in  $\text{NH}_4\text{HO}$ , with which it combines, giving rise to a dangerous compound (fulminating silver), the composition of which has not been ascertained with certainty; by some it is supposed to be a compound of  $\text{Ag}_2\text{O}$  and  $\text{NH}_3$ , by others an amide or nitride of silver. AgCl, when strongly heated, melts, and on cooling has the appearance of *horn*, from which circumstance it has been named *horn silver*. If recently precipitated and still moist AgCl is boiled with excess of KHO, it is converted into  $\text{Ag}_2\text{O}$ . By the action of light argentic salts turn black, and are readily decomposed, Ag

being separated; if any oxidizable matter is present, and even when no organic matter is present, many of them acquire a violet tint, and ultimately turn black. Silver forms the best surface for reflectors by reason of its superior power for reflecting light. Pure silver is unfitted for the manufacture of coins or other articles intended for useful purposes, owing to its softness; it is, therefore, alloyed with a small quantity of Cu, which increases its hardness without affecting its color much; the proportion of Cu in the "standard" silver employed for coinage varies in different countries; in England it amounts to 7.5 per cent., and in France to 10 per cent. Silver solder is an alloy of Ag, Cu, and Zn, containing about 66 per cent. of Ag.

306. The principal minerals of this metal are the SULPHIDE (*silver glance*,  $\text{Ag}_2\text{S}$ ), the CHLORIDE (*horn silver*,  $\text{AgCl}$ ), SULPHIDE OF SILVER and ARSENIC ( $3\text{Ag}_2\text{S} + \text{As}_2\text{S}_3$ ), and SULPHIDE OF SILVER and ANTIMONY ( $3\text{Ag}_2\text{S} + \text{Sb}_2\text{S}_3$ ); SILVER is also met with in the metallic state. It is likewise found in small quantities in most lead and copper ores.

307. When silver compounds, mixed with *carbonate of soda*, are subjected on charcoal to the inner blowpipe flame, brilliant metallic globules are produced, which are not attended with any incrustation.

308. "If silver occurs only in traces in slags or complex ores, it can only be detected by the well-known method of cupellation. If, however, the silver compound is not mixed with a very large amount of foreign matter, it can be detected in very minute quantities by reduction with soda on the charcoal splinter. The white ductile beads dissolve easily on warming in dilute  $\text{HNO}_3$ , and yield  $\text{AgCl}$  with  $\text{HCl}$ , which can then readily be recognized by its behavior with  $\text{HNO}_3$  and  $\text{NH}_4\text{HO}$ . Less than one-tenth of a milligramme of silver can thus be easily detected with certainty."—*Bunsen*.

*Characteristic reactions.*—That with  $\text{HCl}$  and the solubility of the  $\text{AgCl}$  in  $\text{NH}_4\text{HO}$ .

309. Ag forms at least one other oxide, the neutral peroxide,  $\text{Ag}_2\text{O}_2$ , which is formed by decomposing by the voltaic current a weak solution of  $\text{AgNO}_3$ ; there is also some reason to believe in the existence of a suboxide  $\text{Ag}_2\text{O}$ . Both these oxides, if the latter exists, are decomposed by acids, argentic salts being formed.

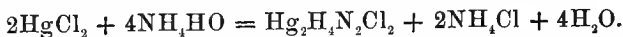
310. *Hg and its compounds.*—Hg is the only metal that is fluid at common temperatures. It freezes at  $-39^\circ$ , and



boils at  $350^{\circ}$  C. It enters into combination with Cl and Br at ordinary temperatures. It combines with I and S in the cold, if triturated with them. Hl and  $H_2S$  are slowly decomposed by it, H being evolved. It combines with most of the metals at ordinary temperatures, forming alloys which are termed amalgams.  $Hg_2O$  is so unstable that it is decomposed even when dry on exposure to diffuse daylight into HgO and Hg. HgO is obtained in the form of red scales by the ignition of  $Hg(NO_3)_2$ , and in the form of a bright yellow powder by adding KHO to solutions of mercuric salts. When the scales are heated they become nearly black, but on cooling the red color returns. HgO forms a soluble compound with BaO.  $H_2C_2O_4$  combines with the yellow oxide in the cold, but does not act on the red oxide; an alcoholic solution of  $HgCl_2$  converts the yellow oxide into the black oxychloride, but it does not act on the red oxide. When  $NH_4HO$  is added to the yellow oxide, a yellowish-white amorphous powder is produced, which is the hydrate of a powerful base, mercuramine ( $Hg_4H_4N_2O_3, 3H_2O$ ). The precipitate produced by  $K_2CO_3$  in solutions of  $HgCl_2$  is the yellow oxide; that by  $KHCO_3$  is the red oxychloride.

311. The fixed alkalies, like  $NH_4HO$ , change  $HgCl$  into a *black* compound; but the compound produced by the action of the fixed alkalies on  $HgCl$  is  $Hg_2O$ , whilst the compound produced by  $NH_4HO$  is, as is shown in the table, dimercurous-ammonic chloride. The following is the reaction:  $2HgCl + 2NH_4HO = Hg_2H_2NCl + NH_4Cl + 2H_2O$ .  $NH_3$  is absorbed by  $HgCl$ , mercurous-ammonic chloride being formed, thus:  $HgCl + NH_3 = HgH_3NCl$ .

312.  $NH_4HO$ , added in *excess* to a solution of  $HgCl_2$ , produces a white precipitate of dimercuric diammonic dichloride ( $Hg_2H_4N_2Cl_2$ ). This substance is used in medicine under the name "*white precipitate*." The action of  $NH_4HO$  on the two mercury chlorides is very analogous. The following is the reaction on  $HgCl_2$ :—



If on the addition of  $NH_4HO$  to the  $HgCl_2$  solution the latter is maintained in considerable *excess*, the precipitate has a different composition to what it has in the preceding case. The *empirical* formula of the precipitate in this latter case is  $Hg_4H_4N_2Cl_6$ ; its *rational* formula may be  $Hg_2H_4N_2Cl_2 + 2HgCl_2$ , a double salt, composed of one

equivalent of dimercuric diammonic dichloride and two equivalents of mercuric chloride.

313. For the action of soluble iodides on mercurous and mercuric salts see pars. 478 and 479.

314. The presence of Hg may be detected in solution by placing in it a small strip of Zn, round which a thin strip of gold foil is twisted. The Hg will be deposited on the Au by voltaic action in the form of a *white stain*, which disappears on heating the Au to redness.

315. Cu, introduced into a solution of a mercurous or a mercuric salt, especially after adding HCl, becomes covered with a white lustrous coating; when moderately heated, the Cu regains its original color, vapors of Hg being evolved: this test is exceedingly delicate. Slips of copper wire, about an inch in length, may be used; they should be cleaned by shaking for a few moments with concentrated  $\text{HNO}_3$ , and thoroughly washed. Half a dozen such slips should be boiled for three or four minutes in the solution, previously acidulated with HCl; they are then well rinsed, dried by pressure between blotting-paper, and heated in a glass tube of one-quarter of an inch diameter, constructed so as to allow the passage of a feeble current of air. A coating of minute *globules* of Hg is formed upon the cool part of the tube; these may be united into larger globules by rubbing with a glass rod. The copper wire being removed, a very minute particle of I may be introduced into the tube, and a gentle heat applied to vaporize it. The sublimate of Hg will thus be converted into  $\text{HgI}_2$ , which is yellow at first, and becomes scarlet when rubbed with a glass rod.

316. If  $\text{SnCl}_2$  be added in small quantity to mercuric salts, it reduces them to mercurous salts, and, as a consequence,  $\text{HgCl}$  precipitates; but if it be added in excess, the mercury salt (mercurous as well as mercuric) is completely decomposed, Hg being thrown down as a gray precipitate, which may be united into globules by heat and agitation—but most readily by boiling the metallic deposit, after decantation of the supernatant fluid, with HCl.

317. *Detection of Hg in organic liquids.*—Acidify with a few drops of HCl; add a few strips of copper wire or foil, and boil for about half an hour; then remove the Cu from the liquid and wash it with a little dilute solution of  $\text{NH}_4\text{HO}$ , so as to remove any copper oxide; then dry it by gentle pressure between folds of bibulous paper, and examine it according to par. 315.

318. *Detection of Hg in organic solids.*—The solid cut into small pieces is heated with  $\text{HCl}$  and  $\text{KClO}_3$ , as directed in par. 733; after being boiled for a few minutes, it must, after cooling, be filtered, and the filtrate evaporated to a small bulk; if any solid separates during the evaporation, it is again filtered, washed  $\text{H}_2\text{S}$  is passed through the concentrated fluid; if a black precipitate is formed, it must be collected upon a filter, and washed with  $\text{H}_2\text{O}$  until all  $\text{Cl}$  is removed, and then purified by boiling it in dilute  $\text{HNO}_3$ ; it is afterwards dissolved in as small a quantity of aqua regia as possible, and examined for  $\text{Hg}$  according to par. 296—2d.

319. Solid compounds of  $\text{Hg}$ , mixed with a large excess (at least twelve parts) of dry  $\text{Na}_2\text{CO}_3$ , and heated in a perfectly dry tube of hard glass, having a diameter of about one-quarter of an inch, and expanded into a bulb at one end, furnish minute *globules*,  $\text{Hg}$ , which are deposited on the cool part of the tube and may be united into larger globules by rubbing with a glass rod. This test is exceedingly delicate; in order that it may be perfectly successful, the  $\text{Hg}$  compound should be thoroughly dried (in a water bath), and the  $\text{Na}_2\text{CO}_3$  should be ignited immediately previous to use. In order to prevent the sublimation of undecomposed  $\text{Hg}$  compounds, it is well to cover the mixture in the bulb-tube with a layer of pure  $\text{Na}_2\text{CO}_3$ .

320. The chief mineral of this metal is the MERCURIC SULPHIDE (*cinnabar*); it is likewise met with in the metallic state.

321. *Flame reactions.*—(a) *Metallic film* is mouse-gray, noncoherent, and spreads over the whole basin. To obtain small traces of  $\text{Hg}$  in the reduced state, the sample is mixed with soda and  $\text{KNO}_3$  and filled into a thin test-tube five to six millims. wide and ten to twenty millims. long. This is held by a  $\text{Pt}$  wire in the flame, whilst the bottom of the basin, filled with cold water, is placed close above the open end of the tube. If the quantity of  $\text{Hg}$  is considerable, it collects in the form of globules, which can be seen with a lens, and which can be collected into larger drops by wiping the basin with a piece of moistened filter-paper.

(c) *Iodide-film* is obtained by breathing on the metallic film, and then placing it over the vessel (fig. 8 of the *Plate*) containing moist  $\text{Br}$ . It first becomes black, and then disappears, but not until after some time;  $\text{HgBr}_2$  is formed. If the basin be now placed above the vessel of fuming  $\text{HI}$ , a very characteristic carmine-colored film of  $\text{HgI}_2$  is pro-

duced ; this is often accompanied by  $\text{HgI}$ , but neither of these disappears on breathing, nor when blown with ammoniac air.

(d) *Sulphide-film* black, not altered by breathing or by blowing with  $(\text{NH}_4)_2\text{S}$ .—*Bunsen*.

*Characteristic reactions*.—For mercurous compounds those with  $\text{HCl}$  and  $\text{NH}_4\text{HO}$ . For mercuric compounds those with  $\text{KI}$ ,  $\text{NH}_4\text{HO}$ , and  $\text{KHO}$

322. No other oxides of  $\text{Hg}$  are known.

323. *Bi and its compounds*.—The color of  $\text{Bi}$  is reddish-white ; it is hard and brittle, and when pure crystallizes more readily than any other metal. It melts at  $264^\circ \text{C}$ ., and it volatilizes at high temperatures. If projected into an atmosphere of  $\text{Cl}$  it takes fire ; it also unites readily with  $\text{I}$ ,  $\text{Br}$ , and  $\text{S}$ .  $\text{Bi}_2\text{O}_3$  melts at a red heat ; it and the *hydrate* are both readily soluble in dilute mineral acids. The hydrate is dehydrated on boiling it in solutions of  $\text{KHO}$ . Many of the bismuthic salts crystallize well, but they cannot exist in solution unless an excess of acid is present, as they are decomposed by water (and this is one of their distinguishing characters) into insoluble basic and soluble acid salts ; this property is exhibited in the most decided manner by the chloride.  $\text{Bi}$  is found principally in the metallic state. Pewter and Britannia metal are alloys of  $\text{Cu}$ ,  $\text{Sn}$ ,  $\text{Sb}$ , and  $\text{Bi}$ . Newton's fusible metal and the metal for calico-printing blocks are alloys of  $\text{Sn}$ ,  $\text{Pb}$ , and  $\text{Bi}$ .

324. The decomposition of the chloride by  $\text{H}_2\text{O}$  is employed as a confirmatory test for  $\text{Bi}$ . The precipitate produced by  $\text{NH}_4\text{HO}$  is dissolved in a small quantity of  $\text{HCl}$ , evaporated to all but dryness, and is then poured into a large quantity of water ; when  $\text{Bi}$  is present, a milky turbidness will be produced.

325.  $\text{K}_2\text{CrO}_4$  throws down from solution of  $\text{Bi}$  the **YELLOW CHROMATE**.  $\text{Bi}_2(\text{CrO}_4)_3$  differs from  $\text{PbCrO}_4$  by its solubility in dilute  $\text{HNO}_3$ , and its insolubility in  $\text{KHO}$ .

326. For detecting  $\text{Bi}$  in the presence of  $\text{Pb}$ , see par 337.

327. When bismuth compounds mixed with  $\text{Na}_2\text{CO}_3$  are exposed on charcoal to the inner blowpipe flame, brittle metallic globules are obtained, attended with a yellow incrustation of  $\text{Bi}_2\text{O}_3$ .

328. *Flame reactions*.—(b) *Reduction-film* black, dead or brilliant ; thin portion of film brownish-black.

(c) *Oxide-film* light yellow ; unaltered by  $\text{AgNO}_3$  with

or without ammonia; gives no reaction with  $\text{SnCl}_2$ , but yields black precipitate of  $\text{Bi}_2\text{O}_3$  on addition of  $\text{NaHO}$ .

(d) *Iodide-film* is very characteristic, and remarkable for the number of tints which it assumes. The thick part is of a brown or blackish-brown color, with a shade of lavender blue; the thin film varies from flesh color to light pink; it easily disappears on breathing, and appears again on blowing. In a stream of ammoniac air it passes from pink to orange, and on blowing or warming it again attains a chestnut-brown color; it resembles the oxide-film in its behavior with  $\text{SnCl}_2$  and  $\text{NaHO}$ .

(e) *Sulphide-film* is of a burnt number color; the thin parts are of a lighter coffee-brown color, does not disappear on blowing, and is not soluble in  $(\text{NH}_4)_2\text{S}$ .

(f) *On charcoal splinter with soda* the bismuth compounds are reduced to a metallic bead, yielding, when rubbed in the mortar, bright, shining, yellowish splinters of metal soluble in  $\text{HNO}_3$ . The solution gives, with  $\text{SnCl}_2$  and  $\text{NaHO}$ , black  $\text{Bi}_2\text{O}_3$ .

*Characteristic.*—The decomposition of the chloride by water, the reaction with  $\text{K}_2\text{CrO}_4$ , and the flame reactions.

329. Three other oxides of Bi are known, viz. bismuthic anhydride ( $\text{Bi}_2\text{O}_5$ ), also  $\text{Bi}_2\text{O}_4$ , which may be regarded as a compound of  $\text{Bi}_2\text{O}_3$  and  $\text{Bi}_2\text{O}_5$ , and a dioxide,  $\text{Bi}_2\text{O}_2$ . The first of these oxides is obtained by passing Cl into a strong solution of KHO, in which is suspended bismuthous hydrate; a blood-red solution of potassic bismuthate and a red precipitate is formed. The red precipitate is digested in  $\text{HNO}_3$  to remove the bismuthous oxide, with which it is always mixed; a red powder is left, which is bismuthic acid,  $\text{HBiO}_3$ . By a heat of  $270^\circ$  it is rendered anhydrous, and assumes a brown color. At a somewhat higher temperature it loses oxygen, and becomes converted into the second oxide,  $\text{Bi}_2\text{O}_4$ .  $\text{Bi}_2\text{O}_4$  is obtained by treating equivalent quantities of  $\text{BiCl}_3$  and  $\text{SnCl}_2$  with an excess of KHO, filtering and drying in an atmosphere of CO; it is black in color, and takes fire when heated in the air, being converted into  $\text{Bi}_2\text{O}_3$ .

230. *Cd and its compounds.*—This metal is of a white color; it is soft, it melts below a red heat; it is more volatile than Zn, and it volatilizes somewhat below the boiling-point of Hg.  $\text{CdO}$  is quite fixed in the fire, and does not melt at the strongest white heat.  $\text{CdO}$  and its hydrate are both easily soluble in dilute mineral acids; most of the salts of Cd are soluble in water. Cd occurs only in

zinc ores. It is found as sulphide in zinc blende, and as oxide or carbonate in calamine.

331. When compounds of Cd, mixed with  $\text{Na}_2\text{CO}_3$  or other reducing agents, are exposed on charcoal to the inner blowpipe flame, the charcoal becomes covered with a yellow or reddish-yellow incrustation of  $\text{CdO}$ .

332. *Flame reactions*.—(a) *Metallic-film* black; the thin parts brown.

(b) *Oxide-film* brownish-black, shading off through brown to a white invisible film of suboxide, which is not altered by stannous chloride, either alone or with soda;  $\text{AgNO}_3$  produces a blackish-blue coloration of reduced metal, which is very characteristic and does not disappear on addition of  $\text{NH}_4\text{HO}$ .

(c) *Iodide-film* white, no change produced by  $\text{NH}_4\text{HO}$ .

(d) *Sulphide-film* lemon-yellow, insoluble in ammonia.

(e) *Reduction on charcoal splinter with soda*.—The metal, owing to its volatility, can only with difficulty be obtained as a silver-white ductile bead.

*Characteristic reactions*.—The color of the sulphide and the flame reactions.

333. Cd forms another oxide,  $\text{Cd}_2\text{O}$ ; it is obtained by heating  $\text{CdC}_2\text{O}_4$ ; it is a green powder, and is decomposed by heat or acids into Cd and  $\text{CdO}$ .

334. *Pb and its compounds*.—Pb is of a bluish-white color; when cut, the fresh surfaces have considerable lustre; it is very soft, malleable, and ductile; it leaves a streak upon paper; it fuses completely at  $327^\circ \text{C}$ ., and at a red heat gives off vapors. It combines directly with S, P, and As, and alloys with most of the metals. The chief of the useful alloys of which this metal is a constituent have already been noticed. It is readily oxidized by  $\text{CuO}$ , which is reduced to the state of  $\text{Cu}_2\text{O}$ .  $\text{PbO}$  in commerce frequently goes under the name of *massicot*, and when partially fused is called *litharge*.  $\text{PbO}$  melts readily at a low red heat, and dissolves glass and earthenware, forming readily fusible silicates. It has a considerable affinity for acids; the best solvent both for it and the hydrate is  $\text{HNO}_3$  or acetic acid; the hydrate speedily absorbs  $\text{CO}_2$  from the air. Oxide of lead dissolves in 7000 parts of pure water; its *solubility* is greatly diminished in the presence of certain salts, sulphates, phosphates,\* and carbonates for

\* Dr. Frankland has recently observed that water which dissolves lead ceases to do so after it has been passed through animal charcoal, by

example, and *increased* by  $\text{NH}_4\text{HO}$  and its salts. Metallic lead undergoes no change when sealed up in pure water, from which the air has been expelled by boiling. It is oxidized, however, when exposed to the influence both of air and water; the oxide thus formed dissolves in the water, and this solution absorbs  $\text{CO}_2$  from the air; a film of hydrated carbonate of lead,  $\text{PbH}_2\text{O}_2 \cdot \text{PbCO}_3$ , is thus formed which is deposited in silky scales. Another portion of oxide becomes formed on the surface of the metal, which is also dissolved by the water, and thus a rapid solution of the metal ensues. This action is materially modified when certain salts exist in the water, even when they do not exceed three or four grains in the gallon. The solvent action is *increased* by the presence of chlorides and nitrates, but is diminished when sulphates, phosphates, or carbonates are present, the  $\text{PbO}$  being scarcely soluble in water containing these latter salts. Acid carbonate of lime is remarkable for its preservative influence, and in consequence of the presence of this salt in most spring water these waters do not act on lead to any serious extent, a film of carbonate of lead being deposited on the surface of the metal and protecting it from further action. The presence of nitrogenous organic matter in water is dangerous, as nitric acid may be formed by its oxidation. As lead is so constantly employed in making cisterns, pipes, etc., for domestic purposes, the action of water on this metal is very important in a sanitary point of view.

335. The principal minerals of this metal are the SULPHIDE (*galena* or *lead glance*,  $\text{PbS}$ ) and the CARBONATE ( $\text{PbCO}_3$ ).

336.  $\text{K}_2\text{CrO}_4$  produces, in solutions of  $\text{Pb}$ , a yellow precipitate of  $\text{PbCrO}_4$ , insoluble in  $\text{HNO}_3$ , but soluble in the fixed alkalies, from which solutions  $\text{PbCrO}_4$  is precipitated on adding acetic acid in excess.

337. When  $\text{KI}$  is added to a solution of a salt of  $\text{Pb}$ , yellow  $\text{PbI}_2$  is precipitated, which dissolves on heating the liquid, and is re-precipitated on cooling in *brilliant golden-colored scales*.\* The solution of the amorphous iodide may be greatly facilitated by the addition of a small quan-

reason of its having dissolved some of the phosphate of lime in the charcoal.

\*  $\text{PbI}_2$  is very soluble in solutions of the acetates of soda, potash, and ammonia, even in the cold, forming colorless solutions, from which  $\text{KI}$ , added in excess, precipitates  $\text{PbI}_2$  in the crystalline state, although no heat has been applied.

tity of  $\text{HCl}$ . If the *least trace* of  $\text{Bi}$  is present in the lead salt, the re-precipitated scales are *no longer yellow*, but assume a *dark orange* or *crimson* tint, varying in intensity of color according to the amount of  $\text{Bi}$  present. This test for  $\text{Bi}$  is of extraordinary delicacy.

338. *Detection of Pb in waters.*—Place two beakers on white paper, side by side; pour into each a pint of the water to be examined; add a little pure  $\text{HCl}$  to the water in one of the beakers, and subsequently some  $\text{H}_2\text{S}$ ; if, after the addition of the  $\text{H}_2\text{S}$ , the water becomes browner in color than the water to which no  $\text{H}_2\text{S}$  has been added, lead is indicated; by this method a quarter grain of lead in a gallon of water can be detected. As organic matter interferes with the reaction, it is necessary to evaporate the water, if it contains much organic matter, to dryness with a few drops of  $\text{HNO}_3$ , and ignite the residue; to the residue afterwards should be added some  $\text{HC}_2\text{H}_3\text{O}_2$  and water, and the mixture heated, and, if necessary, filtered, and to the filtered or unfiltered liquid  $\text{H}_2\text{S}$  should be applied.

339. *Detection of Pb in organic mixtures.*—If the mixture is in the liquid state, a little  $\text{HNO}_3$  is added, and the mixture must be then filtered, and washed  $\text{H}_2\text{S}$  passed through the filtered liquid to excess; a dark-colored precipitate will be formed if lead is present. When a dark-colored precipitate is formed, it is allowed to subside, it is then collected on a filter, and after being thoroughly washed with water, it is dissolved in  $\text{HNO}_3$ , and the solution tested for lead according to 336.

340. *If the mixture is in the solid form*, it may either be heated with  $\text{HCl}$  and  $\text{KClO}_3$ , as described at par. 733, or it may be dried, and the dried mass heated to dull redness until the ash is of a gray color; it is then dissolved in dilute  $\text{HNO}_3$ , and treated with  $\text{H}_2\text{S}$ , etc., as in the preceding case.

341. When lead compounds, mixed with  $\text{Na}_2\text{CO}_3$ , are exposed upon charcoal to the inner blowpipe flame, ductile metallic globules are formed, accompanied with an incrustation which is yellow whilst hot, but becomes paler on cooling.

342. *Flame reactions of plumbic compounds.*—(a) *They color the flame pale blue.*

(b) *Reduction film* black, dead or brilliant.

(c) *Oxide-film* bright yellow-ochre-colored; stannous chloride gives no reaction even on addition of  $\text{NaHO}$ ;



$\text{AgNO}_3$  does not produce any reaction, either alone or on addition of  $\text{NH}_4\text{HO}$ .

(d) *Iodide-film* orange- to lemon-yellow, insoluble on breathing or on moistening; disappears on blowing with ammoniacal air, and again appears on warming.

(e) *Sulphide-film* brownish-red to black: by blowing or moistening with  $(\text{NH}_4)_2\text{S}$  it remains unaltered.

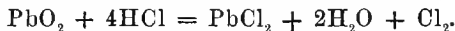
(f) *On charcoal splinter with soda* gives a gray, very soft, ductile metallic bead, which is slowly but completely soluble in  $\text{HNO}_3$ , yielding a white easily crystallizable salt, soluble in  $\text{H}_2\text{O}$ , and precipitated as a white powder on addition of  $\text{H}_2\text{SO}_4$  from a capillary tube.

*Characteristic reactions.*—Those with  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ,  $\text{K}_2\text{CrO}_4$ , and  $\text{H}_2\text{S}$ .

343. Although  $\text{PbO}$  is the only lead oxide which forms salts with acids, three other oxides are known, viz.  $\text{Pb}_2\text{O}$  (black suboxide),  $\text{PbO}_2$  (binoxide), and red lead, which is a compound of the two oxides,  $\text{PbO}_2$  and  $\text{PbO}$ ; its composition varies, but  $2\text{PbO}$ ,  $\text{PbO}_2$  represents an average composition.  $\text{Pb}_2\text{O}$  is obtained by heating  $\text{PbC}_2\text{O}_4$  cautiously in a retort, from which air is excluded; it is converted with acids into plumbic salts. Red lead is obtained by keeping  $\text{PbO}$ , at a dull-red heat, in contact with the air for a considerable time; it is decomposed at a red heat into  $\text{PbO}$  and  $\text{O}$ ;  $\text{HNO}_3$  decomposes it, dissolving out  $\text{PbO}$ , and leaving  $\text{PbO}_2$ .  $\text{PbO}_2$ , sometimes called puce oxide, is a brownish-black substance; it may be obtained, as we have noticed, by treating red lead with  $\text{HNO}_3$ ; it may be prepared in many other ways—it may be obtained, for instance, by adding to  $\text{PbO}$  or  $\text{Pb}_2\text{A}$ , in the presence of water,  $\text{Cl}$  or  $\text{CaOCl}$ ; it is decomposed by heat into  $\text{PbO}$  and  $\text{O}$ ;  $\text{SO}_2$  converts it into  $\text{PbSO}_4$ ; it is often employed in the laboratory to absorb  $\text{SO}_2$ ;  $\text{H}_2\text{SO}_3$  converts it into  $\text{PbSO}_4$ , thus:—



treated with concentrated  $\text{HCl}$  in the cold, or heated with dilute  $\text{HCl}$ , it is converted into  $\text{PbCl}_2$ , thus:—



344. *Cu and its compounds.*—This metal is of a red color. In the finely divided state it is a soft, dark red, dull-looking powder. If exposed to a very intense heat it volatilizes, but it is usually considered fixed in the fire. It is an excellent conductor of heat and electricity, standing in

this respect next to Ag. In the state of foil or filings it takes fire in an atmosphere of Cl. At ordinary temperatures, and at a *red* heat, it unites directly with Br, I, S, Si, etc. Concentrated HI dissolves it readily,  $H_2$  being evolved. The fixed alkalis have little or no action on it, but  $NH_4HO$  gradually dissolves it if exposed to the air; the compound in solution, which is of a deep blue color, has the formula  $CuO(NH_3)_2$ ; a nitrate is formed at the same time. Cu, introduced into a gas or alcoholic flame, communicates to it a *green color*.  $CuO$  and its hydrates dissolve with facility in the mineral acids, even in their diluted state. If  $CuO$  is gently ignited with Cu, there is formed  $Cu_2O$ . When  $CuO$  is boiled with  $SnCl_2$ ,  $SnO_2$  is precipitated, and  $CuCl$  dissolved. With P at a red heat,  $CuO$  yields phosphide and phosphate of copper.  $CuO$  appears to unite with ammonia in more than one proportion. When  $NH_4HO$  is not added in excess to cupric salts, a basic cupric salt, free from ammonia, is usually precipitated.  $NH_4HO$  added to  $CuSO_4$  produces at first a basic cupric sulphate, which dissolves on the addition of more  $NH_4HO$ , forming a deep blue solution, which may be considered as containing ammoniac sulphate in combination with ammoniac cuprate, having the following formula:  $(NH_3)_4Cu$ . Cu is a constituent of many useful alloys, the chief of which have been already noticed under the heads of the other metals. If bright metallic iron be introduced into copper solutions, it becomes coated with a red deposit of that metal, provided the solution be neutral or only very slightly acid.

345. This metal is sometimes found in the native state, but it chiefly occurs in combination with iron sulphide, constituting the COPPER PYRITES ( $Cu_2S + Fe_2S_3$ ), and in BLUE COPPER ORE, or MALACHITE ( $CuCO_3, CuO, H_2O$ ).

346.  $K_4Fe''Cy_6$  throws down, even from dilute solutions of copper, a reddish-brown precipitate of  $Cu_2Fe''Cy_6$ , which is insoluble in dilute acids, is decomposed by the fixed alkalis, is soluble in  $NH_4HO$ , which solution has a deep blue color.

347. *Detection of copper in organic liquids.*—Acidulate with HCl, introduce a piece of polished iron (344), and allow it to remain in the liquid several hours if no perceptible deposition takes place in a shorter time. If any doubt exists about the deposit, examine either a portion of the solution which has not had the iron test applied to it, or by dissolving some of the precipitate, which has been scraped

off the iron, in  $\text{HNO}_3$ , and examining that or the original solution with  $\text{NH}_4\text{HO}$  or  $\text{K}_4\text{Fe}''\text{Cy}_6$ .

348. *Detection in organic solids.*—The substance to be examined is cut into small pieces, and treated with  $\text{HCl}$  and  $\text{KClO}_3$ , as directed at par. 733. The acid solution, after filtering it, is evaporated nearly to dryness, and then examined by one or other or by all the following tests:  $\text{Fe}$  (par. 344),  $\text{NH}_4\text{HO}$  (Table VI. W 3),  $\text{K}_4\text{Fe}''\text{Cy}_6$  (par. 346).

349. When any copper compounds, mixed with  $\text{Na}_2\text{CO}_3$ , are exposed on a charcoal support to the inner blowpipe flame,  $\text{Cu}$  is obtained, unaccompanied with any incrustation on the charcoal.

350. *Flame reactions.*—(a) *On the charcoal splinter with soda* the copper compounds yield a ductile lustrous metallic bead, easily recognizable by its red copper color. By rubbing in the mortar, flat metallic particles are obtained, which can be readily washed, and are easily soluble in  $\text{HNO}_3$ . The blue solution, absorbed on filter-paper, yields a brown stain on addition of  $\text{K}_4\text{Fe}''\text{Cy}_6$ . Instead of acting upon a metal in a curved glass, it may be dissolved by moistening paper upon which it is placed with  $\text{HNO}_3$ .

(b) *With borax on platinum wire.*—Blue bead, not altered to cuprous oxide when heated in the lower reducing flame alone, but on addition of very little tin-salt forms a reddish-brown bead. If this bead be frequently oxidized and reduced in the flame, a ruby-red transparent bead is obtained; this occurs most readily when the bead is allowed to oxidize very slowly.—*Bunsen*.

*Characteristic reactions.*—Those with  $\text{NH}_4\text{HO}$  and  $\text{K}_4\text{FeCy}_6$ .

351. Three other oxides of copper are known, viz.  $\text{Cu}_2\text{O}$ ,  $\text{Cu}_4\text{O}$ , and  $\text{Cu}_2\text{O}_3$ ; there is very little known about the last two. We have already noticed the formation of the first oxide,  $\text{Cu}_2\text{O}$  (par. 257), and we shall learn hereafter some other methods for its formation; it is of a red color, and its solution in  $\text{HCl}$  absorbs  $\text{O}$  rapidly, and becomes converted into a cupric salt. One of the most remarkable properties of the solutions of this oxide in  $\text{HCl}$  is that of absorbing  $\text{CO}$ , and forming with it a crystalline compound.

352. The following methods have also been proposed for the separation of  $\text{Cd}$  and  $\text{Cu}$ :—

1st Method.—Acidify the solution, if it is not acid, with  $\text{HCl}$ ; then pass  $\text{H}_2\text{S}$  through the solution. The two metals, if present, will be precipitated as sulphides; the precipitate

must be well washed, and then boiled with dilute  $\text{H}_2\text{SO}_4$ . The  $\text{CdS}$  is decomposed by the  $\text{H}_2\text{SO}_4$ ,  $\text{CdSO}_4$  being formed, which dissolves, whilst the  $\text{CuS}$  is undecomposed and undissolved. Separate the two by filtration, test the filtrate for  $\text{Cd}$  by  $\text{H}_2\text{S}$ ; dissolve the  $\text{CuS}$  in  $\text{HNO}_3$ ; neutralize with  $\text{NH}_4\text{HO}$ , acidify with acetic acid, then add  $\text{K}_4\text{Fe}''\text{Cy}_6$ . This is a good method; the only precaution to be attended to is, that the mixed sulphides must be washed rapidly, so that the  $\text{CuS}$  may not become oxidized by exposure to the air.—*Dr. A. W. Hoffman.*

2d Method.—To one portion of the acetic solution add  $\text{H}_2\text{S}$  in excess. The formation of a yellow precipitate denotes  $\text{Cd}$ . If, on account of the presence of  $\text{Cu}$ , the  $\text{CdS}$  cannot be distinctly recognized, allow the precipitate produced by the  $\text{H}_2\text{S}$  to subside, decant the supernatant fluid, and add to the precipitate a solution of  $\text{KC}_y$  until the  $\text{CuS}$  is dissolved. If a yellow residue is left undissolved,  $\text{Cd}$  is present; in the contrary case, not.—*Fresenius.*

353. Answers to the following exercises must be written out:—

#### EXERCISES.

114. If after dissolving the precipitated sulphides of the second division of the sixth group in  $\text{HNO}_3$ , you were to add  $\text{NH}_4\text{HO}$  without first adding  $\text{H}_2\text{SO}_4$ , how would you examine the precipitate for  $\text{Bi}$  and  $\text{Pb}$ ? Describe as many methods as possible.

115. I have some ferrous sulphate which contains some cupric sulphate; how must I precipitate the  $\text{Cu}$ , so that after the precipitation the ferrous sulphate remains perfectly pure?

116. How would you prepare pure argentic nitrate from an alloy of copper and silver?

117. What substances *increase*, and what substances *decrease*, the solvent action of water on lead?

118. What is the action of  $\text{KHO}$  on cupric salts, and how is this action modified in the presence of  $\text{As}_2\text{O}_3$ ?

119. How would you proceed to detect and separate all the members of the sixth group, if you were to precipitate the members of the first as well as those of the second division with  $\text{H}_2\text{S}$ ?

120. A mixture of  $\text{PbS}$  and  $\text{PbSO}_4$ , in the proportion of one equivalent of  $\text{PbS}$  to three of  $\text{PbSO}_4$ , is heated to near the fusing point; what changes take place?

121. Describe the processes for the detection of copper in mixtures containing organic matter.

122. Give the formula of the different lead oxides, and state how they are prepared.

123. A colorless solution is given you which you have to examine for the members of the six groups. What members must be absent?

124. Give the composition of the oxides and chlorides of mercury, and describe by equations the action of the volatile and fixed alkalies upon them; and state how mercurous and mercuric compounds are distinguished from each other.

125. The salts of another metal form, like the cupric salts, a blue solution with  $\text{NH}_4\text{HO}$ ; name the metal, and state how you would distinguish the Cu and this metal from each other in a solution.

126. How would you detect corrosive sublimate in organic mixtures?

127. Give several methods of reducing  $\text{AgCl}$ .

128. The water in copper mines contains Cu and Fe in solution as sulphates, owing to the oxidation of some of the copper ore,  $\text{Cu}_2\text{S}$ ,  $\text{Fe}_2\text{S}_3$ ; the water is pumped into wood spouts, the bottoms of which are covered with pieces of scrap iron. What is the object of passing the mine water over the iron?

129. Some red silver ore,  $3\text{Ag}_2\text{S}$ ,  $\text{Sb}_2\text{S}_3$ , is placed in the bulb of a glass tube; a stream of dry H is passed over it, and it is heated to fusion by means of a lamp; when pure H only escapes from the glass-tube the lamp is removed. What change has the H effected? Dry Cl is afterwards passed through the tube, and a gentle heat applied to the bulb; what change does the Cl effect, and what substance finally remains in the tube?

130. I have in solution arsenious and arsenic acids, and Cu, Ni, Co, and Fe in the ferric state. I diffuse  $\text{CaCO}_3$  through the solution without heating it, and allow it to stand for some time. I then filter off and pass Cl through the filtrate, and again add  $\text{CaCO}_3$ . I again filter, and to the filtrate add lime-water. What change does the  $\text{CaCO}_3$  effect, for what purpose is the Cl added, and of what does the precipitate consist which is produced by lime-water, and why is lime-water added in preference to KHO or NaHO?

131. An ore containing  $\text{CuS}$ ,  $\text{FeS}_2$ , and  $\text{Ag}_2\text{S}$ , is roasted in contact with the air, the heat being gradually raised during the space of three or four hours to a dull red, and

finally to a bright red; the roasted mass is finally heated with water, and metallic copper is introduced into the solution. What changes do the sulphides undergo in the first stages of the roasting, in what state are the metals finally left, and what substances remain undissolved, and what are dissolved by the water and for what purpose is the Cu introduced into the aqueous solution?

132. Different processes have been proposed, and are carried out in the smelting of the sulphur ores of silver; sometimes the  $\text{Ag}_2\text{S}$  is fused with Pb; sometimes it is fused with  $\text{PbSO}_4$ , in equivalent proportions; sometimes it is fused with PbO in the proportion of an equivalent of the  $\text{Ag}_2\text{S}$  to two equivalents of PbO. Show by diagrams the reactions which take place in each case.

133. There is present in solution in  $\text{HCl}$ ,  $\text{Fe}_2\text{Cl}_6$ ,  $\text{CuCl}_2$ ,  $\text{CoCl}_2$ ,  $\text{NiCl}_2$ , and  $\text{H}_3\text{AsO}_4$ . I nearly neutralize the solution with  $\text{Na}_2\text{CO}_3$ . I then add sodic acetate in excess, and boil for some time, and afterwards filter. The filtrate I acidulate with  $\text{HCl}$ , and then pass  $\text{H}_2\text{S}$  through it to excess, and again filter. I boil the filtrate to expel the excess of  $\text{H}_2\text{S}$ , and then pass  $\text{Cl}$  through it to excess, and then diffuse  $\text{CaCO}_3$  through the liquid and allow it to stand for several hours. I afterwards add to the filtrate lime-water. What changes take place on boiling the solution after the addition of the alkaline acetate? What is precipitated by the  $\text{H}_2\text{S}$ , by the  $\text{CaCO}_3$ , and by the lime-water?

134. A silver ore containing  $\text{Ag}_2\text{S}$ ,  $\text{CuS}$ ,  $\text{Fe}_3\text{S}_4$ ,  $\text{NiAs}$ , and  $\text{CoAs}_2$ , after being reduced to powder, is mixed with a tenth of its weight of  $\text{NaCl}$ ; the mixture is afterwards roasted for several hours; when the roasting is complete the ore is raked out and allowed to cool; it is then sifted to separate the fully roasted portion, which is in fine powder, from the imperfectly roasted portion, which is in lumps; the fine powder, along with about a tenth of its weight of scrap-iron, is introduced into casks about half filled with water; the casks are then made to revolve for about two hours; about half its weight of mercury is then introduced into the casks, which are then revolved for about twenty hours. The amalgam and mercury in excess are then separated from the spent material by washing, and the amalgam is afterwards separated from the mercury by filtration; the amalgam is finally placed on trays supported on a tripod, over which is placed a large bell-shaped iron vessel, the bottom of which rests in a vessel into which water is constantly flowing; round the upper part of the bell a fire is

lighted, which brings that part of the bell and its contents to a red heat. What change do the metals undergo in roasting? What change do the iron and mercury effect? And what is the object of placing the amalgam under the iron vessel?

#### THE GENERAL PROPERTIES OF THE DIFFERENT BASIC GROUPS.

354. It will be seen by consulting Table VII., that some of the group-reagents precipitate more than one of the groups; the analysis must therefore be commenced by removing *the group* whose reagent does not precipitate the members of any of the other groups under the same circumstances. Such a course will be adopted, if the reagents are employed in the order observed in the table.

355. FIRST DIVISION OF THE SIXTH GROUP.—The analysis must be commenced by adding to the solution HCl, which precipitates the 1st section of the 6th group if present. When a precipitate is produced, collect it upon a filter, wash it twice with cold water, and then examine it, according to the 1st section of Table VI. and par. 293. The wash-water must be collected with the filtrate. *Before adding the HCl, consult* pars. 376, 377, and 378.

356. The filtrate from the precipitate produced by HCl, or the solution with which that *acid* has failed to give a precipitate, must be examined for *the 2d division of the 6th and the whole of the 5th group*, in the manner described in the next paragraph.

357. SECOND DIVISION OF THE SIXTH AND THE WHOLE OF THE FIFTH GROUP.\*— $\text{H}_2\text{S}^\dagger$  must be passed through the

\* Au and Pt are easily detected in the presence of all the metals (paragraph 331); Northcote and Church, in their "Manual of Analysis," recommend their separation from the solution, before precipitating the other members of the fifth and the members of the sixth group by  $\text{H}_2\text{S}$ ; the following is their plan: The filtrate from the HCl precipitate, or the solution which has failed to give a precipitate, is freed from  $\text{HNO}_3$  (if present) by one or two evaporations on the water-bath with HCl; to the HCl solution, which ought to be concentrated, a reasonable quantity of  $\text{NH}_4\text{Cl}$  solution is added, the liquid is then well agitated and allowed to rest for some hours; if Pt is present, a yellow crystalline precipitate of  $2\text{NH}_4\text{Cl}$ ,  $\text{PtCl}_4$  is formed. The filtrate is mixed with a reasonable quantity of a concentrated solution of  $\text{H}_2\text{C}_2\text{O}_4$ , and moderately heated for some hours. A precipitate consisting of yellow spangles or of a brown-yellow sponge indicates Au. The filtrate is then treated with  $\text{H}_2\text{S}$ .

† If the  $\text{Ag}_2\text{O}$ ,  $\text{PbO}$ , and  $\text{Hg}_2\text{O}$ , had not to be sought for, we must nevertheless add HCl to the solution to render it acid, before adding  $\text{H}_2\text{S}$ , in order to prevent the members of the 3d and 4th groups from being precipitated by that reagent, and to insure the complete precipitation of the fifth group.

solution until it *smells strongly* of  $H_2S$  after it has been shaken and gently warmed for some time; the 2d section of the 6th, and the 5th group, when present, will be precipitated. When a precipitate is produced, collect it upon a filter and wash it with hot water, until the wash-water is no longer acid to test-paper; the wash water need not be collected with the filtrate, but may be thrown away.

358. If the FIFTH GROUP *has not to be examined for*, the *washed precipitate* is at once examined according to Table VI. and par. 294.

359. When the FIFTH GROUP *has to be examined for*, the *washed precipitate* must be treated with boiling solution of  $NaHO$ ; the members of the SIXTH GROUP are *insoluble*, but the members of the FIFTH are *soluble* in  $NaHO$ ; if any of the precipitate is insoluble in it, filter, and treat the *insoluble portion* according to par. 360. *Examine the  $NaHO$  solution for the 5th group according to par. 361.*

360. The portion of the precipitate insoluble in  $NaHO$  must be examined, after it has been well washed, according to Table VI. and par. 294.

361. To the  $NaHO$  solution must be added  $HCl$  in excess. If a precipitate is produced, on the addition of  $HCl$ , the color of which is *white*, this arises merely from the separation of  $S$ , *none of the members of the group being present*; if the precipitate is of a *yellow* or *orange* color,  $Sb_2S_3$ ,  $SnS_2$ , and  $As_2S_3$ ,\* can only be present. If the color of the precipitate is *black*, then all the members of the group must be sought for. The precipitate, after being well washed with hot water, must be examined according to the directions given under the 5th group (par. 213). *Before passing the  $H_2S$  through the solution consult pars. 379, 380, and 381.*

362. The *filtrate* from the  $H_2S$  precipitate, or the *solution* with which it has failed to give a precipitate, must be boiled until a piece of bibulous paper moistened with a solution of a lead salt *does not alter in color* when held over it, a proof that all the  $H_2S$  is expelled. If boiling the liquid causes a separation of  $S$ , the solution, after the  $H_2S$  is expelled, must be filtered, and then examined for the 4th group as directed in the next par.

363. THE FOURTH GROUP.—Before adding to the solution the *general reagent* for this group, a small portion of the solution must be tested for  $FeO$ , by adding to it a few

\* For the color of the sulphides of this group see par. 224.



drops of a solution of  $K_6Fe_2Cy_{12}$ ,\* observing the precautions mentioned in par. 177. When FeO is present the remainder of the solution must be boiled in an evaporating dish with a few drops of  $HNO_3$ , until all the FeO is converted into  $Fe_2O_3$ , which is accomplished when a drop of the solution does not give a blue color with  $K_6F_2Cy_{12}$ . When FeO is not present, the solution does not require to be boiled with  $HNO_3$ , but it may at once be examined for the 4th group as directed in the next par.

364.  $NH_4Cl$  and  $NH_4HO$  must then be added to the solution; the  $NH_4HO$  must be added until the solution smells of it after it has been shaken. Warm the solution after the addition of the  $NH_4HO$ , and when a precipitate is produced collect it upon a filter, wash it with hot water until the wash-water does not turn red test-paper blue; examine it then according to Table IV. and par. 156. *Before adding the  $NH_4Cl$  and  $NH_4HO$  consult pars. 382, 383, and 384.*

365. The filtrate from the precipitate produced by  $NH_4HO$ , or the solution with which it has failed to give a precipitate, must be examined for the THIRD GROUP according to the method described in the next par.

366. THIRD GROUP.†— $(NH_4)_2S$  ‡ must be added to the solution, the liquid must afterwards be shaken and gently heated for some time. *When a precipitate is produced*, collect it upon a filter, and examine it according to Table III. and par. 112. Before filtering the whole of the solution, add to that portion of the liquid which has been filtered, a little more  $(NH_4)_2S$ ; if the reagent produces a further precipitate, add some to the unfiltered as well as to the filtered portion, refilter, and again test the filtrate with it. If the  $(NH_4)_2S$  causes no precipitate in the filtered liquid, proceed with the filtration, as the group has been

\*  $K_6Fe_2Cy_{12}$  precipitates other oxides besides the FeO, but with no other oxide but FeO does it give a blue precipitate.

† Although FeO belongs, on account of its general properties, to this group, we have placed it in the special table of the 4th; because, in separating the groups, it is converted by  $HNO_3$  into  $Fe_2O_3$ —a member of the 4th: we have thought it advisable, therefore, to contrast its special properties with the members of that group.

‡ When the student does not look for the members of the three previous groups, viz. the 6th, 5th, and 4th, he must, before adding  $(NH_4)_2S$  to the solution, add  $NH_4Cl$  and  $NH_4HO$ ; in other words, he must add them to the solution which he has to examine for the members of the 3d group, if they have not been added in the previous course of the analysis. The  $NH_4Cl$  is added, to prevent the precipitation of MgO by  $NH_4HO$ .

TABLE VII.—BEHAVIOR OF THE BASIC GROUPS

FIRST GROUP.	SECOND GROUP.		THIRD GROUP.
$K_2O, Na_2O, (NH_4)_2O.$	<i>First Division.</i> $BaO, SrO, CaO.$	<i>Second Division.</i> $MgO.$	$MnO, ZnO, CoO, NiO, FeO.$
1. <i>HCl does not precipitate the members of this group from their solutions, because their chlorides are soluble.</i>	1. <i>HCl does not precipitate the members of this group from their solutions, because their chlorides are soluble.</i>	1. <i>HCl does not precipitate the members of this group from their solutions, because their chlorides are soluble.</i>	1. <i>HCl does not precipitate the members of this group from their solutions, because their chlorides are soluble.</i>
2. <i>H<sub>2</sub>S does not precipitate the members of this group, either from their NEUTRAL, ACID, or ALEALINE solutions, because their sulphides are soluble.</i>	2. <i>H<sub>2</sub>S does not precipitate the members of this group either from their NEUTRAL, ACID, or ALEALINE solutions, because their sulphides are soluble.</i>	2. <i>H<sub>2</sub>S does not precipitate the members of this group from their NEUTRAL, ACID, or ALEALINE solutions, because their sulphides are soluble.</i>	2. <i>H<sub>2</sub>S does not precipitate the members of this group from their ACID solutions.</i>
3. <i>NH<sub>4</sub>HO does not precipitate either of the other two members of the group.</i>	3. <i>NH<sub>4</sub>HO does not* precipitate the members of this division from their solutions.</i>	3. <i>NH<sub>4</sub>HO precipitates Mg partly from its solutions as <math>MgH_2O_2</math>; the presence of AMMONIC SALTS prevents the precipitation.</i>	3. <i>NH<sub>4</sub>HO precipitates the members of this group as HYDRATES. In an excess of the reagent <math>ZnH_2O_2, CoH_2O_2,</math> and <math>NiH_2O_2,</math> are readily soluble, but <math>MnH_2O_2</math> and <math>FeH_2O_2</math> are insoluble; but the presence of AMMONIC SALTS prevents their precipitation.</i>
4. <i>(NH<sub>4</sub>)<sub>2</sub>S does not precipitate the other two members of this group from their solutions, because their sulphides are soluble.</i>	4. <i>(NH<sub>4</sub>)<sub>2</sub>S does not precipitate the members of this group from their solutions, because their sulphides are soluble.</i>	4. <i>(NH<sub>4</sub>)<sub>2</sub>S precipitates the members of this group from NEUTRAL and ALEALINE solutions, as sulphides.</i>	4. <i>(NH<sub>4</sub>)<sub>2</sub>S precipitates the members of this group from NEUTRAL and ALEALINE solutions, as sulphides.</i>
5. <i>(NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> does not precipitate either of the other two members of this group from their solutions.</i>	5. <i>(NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> precipitates the members of this division from solutions as CARBONATES; the presence of AMMONIC SALTS does not interfere with their precipitation.</i>	5. <i>(NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> precipitates Mg only partly, and the presence of AMMONIC SALTS prevents the precipitation.</i>	5. <i>(NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> precipitates the members of this group; but they are all, with the exception of the Mn and Fe precipitates, readily soluble in an excess of the reagent.</i>
6. <i>Na<sub>2</sub>HPO<sub>4</sub> does not precipitate the other two members of this group from their solutions.</i>	6. <i>Na<sub>2</sub>HPO<sub>4</sub> precipitates the members of this division from NEUTRAL and ALEALINE solutions, as PHOSPHATES.</i>	6. <i>Na<sub>2</sub>HPO<sub>4</sub> precipitates Mg from its NEUTRAL and ALEALINE solutions, as PHOSPHATE; violent agitation promotes the formation of the precipitate. The precipitate is more soluble in hot than in cold water.</i>	6. <i>Na<sub>2</sub>HPO<sub>4</sub> precipitates the members of this group from their NEUTRAL solutions as PHOSPHATES.</i>

\* The bario, strontio, and calcio phosphates and oxalates, and magnesic phosphate, are soluble in dilute mineral acids, but insoluble in water and the alkalis; consequently, when their acid solutions are rendered neutral or alkaline by ammonia, these salts are precipitated; therefore, when baryta, strontia, and lime are in combination with phosphoric and oxalic acids, and when magnesia is in combination with phosphoric acid, they are precipitated.

## WITH THE GENERAL OR GROUP REAGENTS.

FOURTH GROUP.	FIFTH GROUP.	SIXTH GROUP.	
$\text{Al}_2\text{O}_3, \text{Cr}_2\text{O}_3, \text{Fe}_2\text{O}_3.$	$\text{SnO}, \text{SnO}_2, \text{Sh}_2\text{O}_3,$ $\text{As}_2\text{O}_3, \text{As}_2\text{O}_5,$ $\text{Au}_2\text{O}_3, \text{PtO}_2.$	<i>Second Division.</i> $\text{HgO}, \text{PbO}, \text{Bi}_2\text{O}_3,$ $\text{CdO}, \text{CuO}.$	<i>First Division.</i> $\text{PbO}, \text{Ag}_2\text{O}, \text{Hg}_2\text{O}.$
1. <i>HCl does not precipitate the members of this group from their solutions, because their chlorides are soluble.</i>	1. <i>HCl does not precipitate the members of this group from their solutions, because their chlorides are soluble.</i>	1. <i>HCl does not precipitate the members of this division of the group, because their chlorides are soluble.</i>	1. <i>HCl precipitates the members of this division, because their chlorides are insoluble. PbCl is slightly soluble in water; it is more soluble in hot than cold water.</i>
2. <i>H<sub>2</sub>S does not precipitate any of the members of this group from their acid solutions, for FeS is readily soluble in acids, and Al<sub>2</sub>S<sub>3</sub> and Cr<sub>2</sub>S<sub>3</sub> are not formed in the humid way.</i>	2. <i>H<sub>2</sub>S precipitates all the members of this group from their acid solutions, as sulphides.</i>	2. <i>H<sub>2</sub>S precipitates all the members of this group from their NEUTRAL, ALKALINE, and ACID solutions, as sulphides.</i>	
3. <i>NH<sub>4</sub>HO, even in the presence of its salts, precipitates the members of this group as HYDRATES,† which an excess of the reagent does not redissolve.</i>	3. <i>NH<sub>4</sub>HO precipitates some of the members of this group.</i>	3. <i>NH<sub>4</sub>HO precipitates the members of this group; but in an excess of the reagent the Ag, Cd, and Cu precipitates redissolve readily; but the Hg, Pb, and Bi precipitates are insoluble in an excess of the reagent.</i>	
4. <i>(NH<sub>4</sub>)<sub>2</sub>S precipitates the members of this group from their NEUTRAL and ALKALINE solutions; Fe<sup>III</sup> as FeS, Al and Cr as Al<sub>2</sub>H<sub>6</sub>O<sub>6</sub> and Cr<sub>2</sub>H<sub>6</sub>O<sub>6</sub>.</i>	4. <i>(NH<sub>4</sub>)<sub>2</sub>S, if added in excess, does not precipitate the members of this group from their solutions, because their SULPHIDES are soluble in the alkaline sulphides.</i>	4. <i>(NH<sub>4</sub>)<sub>2</sub>S precipitates the members of this group from their NEUTRAL and ALKALINE solutions, as sulphides.</i>	
5. <i>(NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> precipitates the members of this group from their solutions as OXIDES; an excess of the reagent does not redissolve them.</i>	5. <i>(NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> precipitates some of the members of this group, as OXIDES.</i>	5. <i>(NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> precipitates the members of this group from their solutions; and an excess of the reagent does not redissolve them, with the exception of the cupric precipitate.</i>	
6. <i>Na<sub>2</sub>HPO<sub>4</sub> precipitates the members of this group from their NEUTRAL solutions as PHOSPHATES.</i>	6. <i>Na<sub>2</sub>HPO<sub>4</sub> precipitates some of the members of this group from their NEUTRAL solutions, as PHOSPHATES.</i>	6. <i>Na<sub>2</sub>HPO<sub>4</sub> precipitates the members of this group from their NEUTRAL solutions, as PHOSPHATES.</i>	

in combination with these acids by ammonia, from their acid solutions, along with the members of the fourth group.

† When the iron, chromic, and aluminic phosphates are present in a solution, they are precipitated as phosphates, and not as hydrates, by ammonia.

completely precipitated. *Before adding*  $(\text{NH}_4)_2\text{S}$  *to the solution consult* pars. 385, 386, 387.

367. If the *filtrate* from the  $(\text{NH}_4)_2\text{S}$  precipitate, or the *solution* with which it has failed to give a precipitate, has become, from its addition, of a *dark brown* color, the *filtrate* or *solution* must be evaporated and then acidified with  $\text{HCl}$ , and filtered as directed in par. 387.  $\text{NH}_4\text{HO}$  in excess must be added to the *filtrate*, which must then be examined for the SECOND GROUP according to par. 369.

368. If the *filtrate* from the  $(\text{NH}_4)_2\text{S}$  precipitate, or the *solution* with which it has failed to give a precipitate, has not *altered in color*, it can at once be examined for the SECOND GROUP as directed in the next par.

369. FIRST DIVISION OF THE SECOND GROUP.— $(\text{NH}_4)_2\text{CO}_3^*$  must be added to the *solution*; the *solution* must then be gently warmed for some time, *but not boiled*. If one or all of the members of this division are present, a precipitate will be produced by the  $(\text{NH}_4)_2\text{CO}_3$ , especially after warming the *solution*. *When a precipitate is produced*, collect it upon a filter and wash it with hot water, and afterwards examine it according to Table II. and par. 66. *Before filtering the whole of the solution*, add to that portion of the liquid which has been filtered a little more  $(\text{NH}_4)_2\text{CO}_3$ ; if the reagent produces a further precipitate, add some to the unfiltered as well as to the filtered portion, re-filter, and again test the *filtrate* with it. If the  $(\text{NH}_4)_2\text{CO}_3$  causes no precipitate in the filtered liquid, proceed with the filtration, as the group has been completely precipitated. *Before adding the*  $(\text{NH}_4)_2\text{CO}_3$  *consult* pars. 388 and 389.

370. The *filtrate* from the precipitate produced by  $(\text{NH}_4)_2\text{CO}_3$ , or the *solution* with which it has failed to give a precipitate, must be examined for  $\text{Mg}$ ,  $\text{K}$ , and  $\text{Na}$ , as directed in the next par.

371. The *solution* which has to be examined for  $\text{Mg}$ ,  $\text{K}$ ,

\* When the student does not look for the members of the four previous groups, viz. the 6th, 5th, 4th, and 3d, he must, before adding the  $(\text{NH}_4)_2\text{CO}_3$  to the *solution*, add  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{HO}$ ; in other words, he must add them to the *solution* which he has to examine for the members of the second group, if they have not been added in the previous course of the analysis. The  $\text{NH}_4\text{Cl}$  is added to prevent the precipitation of the  $\text{MgO}$  by the carbonate of ammonia; any ammoniac salt may be employed, the acid of which forms no insoluble compound with  $\text{MgO}$  or the other members of the group. If the ammoniac carbonate employed is an acid carbonate, a portion of the alkaline earths is apt to be dissolved by it. The  $\text{NH}_4\text{HO}$  is added to prevent this; it does so by converting it into a neutral carbonate.

and Na must be divided into two parts, which we shall call A and B.

372. The A portion may be employed for the examination for Mg; for this purpose we must add to the solution, which must be quite cold,  $\text{Na}_2\text{HPO}_4$  and also  $\text{NH}_4\text{HO}$ , if this latter reagent is not already present in the solution, the liquid after the addition of the reagent ought to be shaken very violently; and if, after time (one or two hours) has been allowed for the formation of the precipitate, *there is no precipitate, Mg is absent. If there is a precipitate, Mg is present. Before adding  $\text{Na}_2\text{HPO}_4$ , consult pars. 390 and 391.*

373. Examine B for K and Na according to par. 27.

374. When a precipitate has been produced by  $(\text{NH}_4)_2\text{CO}_3$ , one drop of dilute  $\text{H}_2\text{SO}_4$  ought to be added to the B solution before it is evaporated and ignited. The acid is added to remove the minute quantity of Sr, if present, which remains unprecipitated by  $(\text{NH}_4)_2\text{CO}_3$ , as Sr imparts to the flame a color very similar to that produced by K.

375. AMMONIA. A portion of the *original* solution must be examined for ammonia according to par. 24.

PARTICULAR OBSERVATIONS REGARDING THE PRECIPITATES PRODUCED BY THE GROUP REAGENTS, AND THE PRECAUTIONS TO BE OBSERVED IN EXAMINING FOR THE DIFFERENT GROUPS.

376. *Precautions to be attended to in examining for the first section of the Sixth Group.*—Before adding HCl to the solution under examination, it is necessary to ascertain, by test papers, whether the solution is acid, neutral, or alkaline. When it is one of the two former, a few drops of the acid will generally be sufficient; if alkaline, the acid must be added until it is decidedly in excess. When a precipitate is produced, add the acid, drop by drop, until it ceases to increase; then add a few drops more, shake the mixture, and filter. When no precipitate is produced, a few drops of the acid will in most cases be sufficient, since our only object in adding it then is to acidify the solution, in order to prevent the precipitation of the 3d and 4th groups by  $\text{H}_2\text{S}$ . *When evolution of gas takes place on the addition of HCl, examine it for  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ , and HCy, as directed under those heads.*

377. As Ag is not precipitated, under certain circumstances, by HCl—and as a precipitate may be produced

on the addition of  $\text{HCl}$ , in the absence of  $\text{Ag}_2\text{O}$ ,  $\text{PbO}$ , and  $\text{Hg}_2\text{O}$ —it is requisite to notice, 1st, the substances which interfere with the precipitation of  $\text{Ag}$ ; 2d, the substances which may be precipitated, and under what condition the precipitation takes place. 1st. When  $\text{Hg}(\text{NO}_3)_2$  is present in the solution,  $\text{Ag}$ , if present, will not be precipitated by  $\text{HCl}$ , because  $\text{AgCl}$  is soluble in a solution of  $\text{Hg}(\text{NO}_3)_2$ , especially if the solution is hot and concentrated; on the addition of water and cooling, the solution may deposit shining yellowish-white crystals, which are pure  $\text{AgCl}$ . When  $\text{Hg}(\text{NO}_3)_2$  is suspected to be present, ammoniac acetate ought to be added to the solution after the addition of the  $\text{HCl}$ , as this insures the complete precipitation of the  $\text{AgCl}$ . 2d. The precipitate\* may be occasioned by the presence of some salt of  $\text{Sb}$  or  $\text{Bi}$ , as  $\text{SbCl}_3$  and  $\text{BiCl}_3$ , are decomposed by much water into soluble acid and insoluble basic salts. The precipitate† may also arise from the presence of some substance insoluble in water, but soluble in the caustic, carbonated, or sulphurated alkalies, or in an alkaline cyanide—for example, phosphate of alumina, or alumina dissolved in  $\text{NaHO}$ ,  $\text{As}_2\text{S}_3$  dissolved in  $\text{NH}_4\text{HCO}_3$ ,  $\text{Sb}_2\text{S}_3$  dissolved in an alkaline sulphide  $\text{NiCy}_2$  dissolved in an alkaline cyanide,  $\text{AgCl}$  dissolved in  $\text{NH}_4\text{HO}$ ; or the precipitate may be due to silicic acid, some alkaline silicate being present. If the precipitate is due either to  $\text{Sb}$  or  $\text{Bi}$ , it will redissolve on the addition of a few drops more of  $\text{HCl}$ . When silicic acid is the substance thrown down, the precipitate will appear very gelatinous, and will remain undissolved on the further addition of acid; a fresh portion of the original solution must, therefore, be acidulated with  $\text{HNO}_3$ , and evaporated to dryness to render the silicic acid insoluble; the ignited mass may then be digested with dilute  $\text{HNO}_3$ , and filtered.‡ The analysis of the filtrate must then be conducted in the regular way, by adding to it  $\text{HCl}$ , etc. If the precipitate should be due to the presence of any of the other sub-

\* If the  $\text{HCl}$  employed contain a trace of  $\text{H}_2\text{SO}_4$  and  $\text{Ba}$  be present in the fluid under examination, a slight trace of insoluble  $\text{BaSO}_4$  will be formed, which may be distinguished by the difficulty experienced in separating it from the fluid by filtration.

†  $\text{HCl}$  precipitates, of the inorganic acids, boracic acid; and of the organic acids, benzoic and uric acids, if the solution is very concentrated. The two former are dissolved by hot water, and the uric acid by heating with  $\text{HNO}_3$ .

‡ The precipitate left upon the filter must be examined for silicic acid according to the method described under the head of that acid.

stances, a fresh portion of the original solution ought to be taken, and  $\text{HNO}_3$  added to it until it is decidedly acid. If the precipitate does not disappear on the addition of the acid, the solution ought to be warmed; if this should fail to dissolve the precipitate, it must be collected upon a filter, and examined as a substance insoluble in water and acids (see 719).

378. As the  $\text{PbCl}_2$ ,  $\text{AgCl}$ , and  $\text{HgCl}$  are very heavy, they easily separate from the solution; there is, therefore, no need to warm the fluid to effect this object. Indeed, it would be disadvantageous to do so, as a portion of the  $\text{HgCl}$  would be converted into  $\text{HgCl}_2$ , and the greater portion, if not all, the  $\text{PbCl}_2$  would be dissolved.

379. *Precautions to be observed in examining for the second section of the Sixth and the whole of the Fifth Group.*—Before passing  $\text{H}_2\text{S}$  through the solution it will be necessary to dilute it with water, if it be very acid, as the members of the two groups are not readily precipitated as sulphides from very acid solutions. Especially is it very difficult to precipitate  $\text{Cd}$  by  $\text{H}_2\text{S}$  in the presence of much  $\text{HCl}$ . If, therefore, the solution has not been diluted, and  $\text{Cd}$  is present, a yellow precipitate may be obtained on adding  $(\text{NH}_4)_2\text{S}$  to precipitate the 3d group. It must also be observed that if the solution has not been rendered sufficiently acid, some of the  $\text{Zn}$ , if it be present, may be precipitated by  $\text{H}_2\text{S}$ . If on diluting the liquid it becomes turbid, this arises from the presence of some salt of  $\text{Sb}$  or  $\text{Bi}$ ; a few drops of acid will redissolve this precipitate. Arsenic acid is reduced very slowly by  $\text{H}_2\text{S}$ , but  $\text{SO}_2^*$  reduces it rapidly, if assisted by a gentle heat; if, therefore, arsenic acid is present or its presence suspected,  $\text{SO}_2$  ought to be added in excess, the solution then gently warmed for some time, and finally boiled until the excess of  $\text{SO}_2$  is expelled. If  $\text{Zn}$  is present, and the arsenic acid has not been reduced, a precipitate would be produced having this composition,  $\text{ZnAs}_2\text{S}_6$ .

380. If, on the addition of  $\text{H}_2\text{S}$ , no precipitate be produced, it proves the absence of the 2d section of the 6th and the whole of the 5th group. If a precipitate be produced, the color of which is white,† this likewise proves the ab-

\* If  $\text{Ba}$ ,  $\text{Sr}$ , or  $\text{Pb}$  be present, the  $\text{SO}_2$  will give rise to a precipitation of their sulphates; the precipitate should be collected upon a filter, washed, dried, and then examined as a substance insoluble in water and acids, according to 729.

† If  $\text{HNO}_3$  be present in the solution, a thick, tenacious, yellow mass of

sence of these groups, as the white precipitate is merely due to a separation of S, occasioned by some of the  $\text{H}_2\text{S}$  being decomposed by its reducing some higher oxide to a lower degree of oxidation. If the color of the solution, originally *orange* or *yellow*, change to a *green*, after the gas is passed through it, the separation of sulphur is due to the reduction of  $\text{CrO}_3$  to  $\text{Cr}_2\text{O}_3$ ; the white S suspended in the green solution frequently perplexes the student, as it appears at first like a green precipitate. If the separation of S be not attended with any change in color, it is (probably) attributable to the reduction of  $\text{Fe}_2\text{O}_3$  to  $\text{FeO}$ ,  $\text{CrO}_3$  and  $\text{Fe}_2\text{O}_3$  being both found in their lower degree of oxidation after  $\text{H}_2\text{S}$  or any reducing agent has been added to their solutions.

381. If on the first transmission of  $\text{H}_2\text{S}$  through the solution a *white* precipitate be formed, which, on a further addition of the reagent, acquires an *orange color*, and becomes finally *black*, it points out that some mercuric salt is present. If the precipitate, on its first formation, assumes a red or brownish-red color, and becomes finally black, it indicates the probable presence of some lead salt.

382. *Precautions to be observed in examining for the Fourth Group.*—If the  $\text{H}_2\text{S}$  were not expelled before boiling the solution with  $\text{HNO}_3$ , the latter would give rise, by oxidation of the S, to  $\text{H}_2\text{SO}_4$ , which would precipitate Ba and Sr, and possibly Ca, as sulphates, if they were present. Even when  $\text{HNO}_3$  has not to be added to the solution, no  $\text{FeO}$  being present, it is necessary to expel the  $\text{H}_2\text{S}$  before adding  $\text{NH}_4\text{HO}$ , otherwise  $(\text{NH}_4)_2\text{S}$  would be formed, and consequently the third as well as the fourth group would be precipitated. When the solution is very acid, no  $\text{NH}_4\text{Cl}$  need be added, as a sufficient amount of ammoniac salt will be formed on the addition of the  $\text{NH}_4\text{HO}$ .

383. When much  $\text{Cr}_2\text{O}_3$  is present, a small quantity will frequently dissolve in the  $\text{NH}_4\text{HO}$ , and will impart to the fluid a puce-red tint. When this occurs, it is difficult to remove the last traces of Cr from the solution. If warming the solution fail, it is better to disregard it; for if the solution were evaporated to effect the object, a greater or

sulphur will separate, occasioned by the decomposition of the  $\text{H}_2\text{S}$  by the acid. When such is the case, the gas has to be passed through the solution for some time before its characteristic odor will be imparted to the liquid, showing that a sufficient quantity has been added.  $\text{HClO}_3$  and free Cl decompose  $\text{H}_2\text{S}$  in the same way as  $\text{HNO}_3$ .



less quantity of the oxides of Mn, Ni, and Co, if they were present, would be precipitated.

384. The precipitate produced by  $\text{NH}_4\text{HO}$  may consist, in addition to the members of the fourth group, of the following salts: Al,  $\text{Cr}'''$ , Fe, Mn, Ba, Sr, Ca, and Mg, in combination with  $\text{PO}_4$ ; and Ba, Sr, and Ca, in combination with  $\text{C}_2\text{O}_4$ . When the student looks for acids as well as bases, he must examine the precipitate produced by  $\text{NH}_4\text{HO}$ , according to Table V., or pars. 191, 197, or 198. Ba, Sr, and Ca, in combination with F and  $\text{BO}_3$ , may also be precipitated by  $\text{NH}_4\text{HO}$  in minute quantities; but as a sufficient quantity of the bases will always remain in solution, and be precipitated as members of the 2d group, and as the acids will be found in the examination for acids, we have not included these salts in the table.

385. *Precautions to be observed in examining for the Third Group.*—If  $\text{CrO}_3$  and Ba are both present in solution, a substance insoluble in acids is sometimes formed on dissolving the precipitate produced by  $\text{NH}_4\text{HO}$ , or that produced by  $(\text{NH}_4)_2\text{S}$ ; the insoluble substance is  $\text{BaSO}_4$ . A sulphur acid appears to be formed when  $\text{CrO}_3$  is reduced by  $\text{H}_2\text{S}$ , which becomes converted into  $\text{SO}_4$  after some time.

386. The precipitate produced by  $(\text{NH}_4)_2\text{S}$  is very difficult to filter; the filtrate will frequently come through the filter *turbid* for some time; there is no remedy for this but to pass it through the filter until it is perfectly clear. The student must not mistake between a *turbid filtrate* and one which is *perfectly clear but colored*. A filter can only remove what is held in suspension by a liquid, as in the first case; it cannot remove what is dissolved, as in the second case; when the filtrate is colored, consult the next par. The precipitate must be carefully washed with water containing a little  $(\text{NH}_4)_2\text{S}$ , in order to prevent the precipitated sulphides from oxidizing. If the wash-water comes through of a deep-brown color, it must be treated as directed in the next par.

387. If the filtrate from the  $(\text{NH}_4)_2\text{S}$  precipitate be of a very dark brown color, it is occasioned by the presence of Ni, the sulphide of that metal being slightly soluble in  $(\text{NH}_4)_2\text{S}$ . When a considerable portion of this substance has passed into solution, the filtrate, and likewise the wash-water if it is dark colored, must be evaporated until the excess of  $(\text{NH}_4)_2\text{S}$  is expelled; the solution is then acidified with dilute  $\text{HCl}$ , and the black precipitate which separates on the addition of the acid collected upon a filter, and

examined with that previously obtained. If Cd has not been completely precipitated by  $\text{H}_2\text{S}$ , the precipitate by  $(\text{NH}_4)_2\text{S}$  may be yellow in color from the presence of  $\text{CdS}$ .

388. *Precautions to be observed in examining for the first division of the Second Group.*—After the addition of the  $(\text{NH}_4)_2\text{CO}_3$ , the solution should be heated gently, but not boiled, since the  $\text{NH}_4\text{Cl}$  might then decompose and dissolve some of the precipitated carbonates.

389. Although  $(\text{NH}_4)_2\text{CO}_3$  does not precipitate completely Ba, Sr, and Ca from their solutions, especially when the quantity of ammoniac salts present is considerable, it is sufficiently exact for all ordinary qualitative purposes. "The separation is never perfect, owing to the solvent action which ammoniac salts exercise, more especially upon  $\text{BaCO}_3$  and  $\text{CaCO}_3$ ; indeed, minute traces of Ba and Ca can rarely be precipitated in this manner. Ba is separated the most completely by  $\text{H}_2\text{SO}_4$  or a sulphate; Ca by  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  in presence of  $\text{NH}_4\text{HO}$  and some  $\text{NH}_4\text{Cl}$ ; Sr same manner as Ca, or by  $\text{NH}_4\text{HO}$  and  $(\text{NH}_4)_2\text{CO}_3$  in presence of  $\text{NH}_4\text{Cl}$ ."

390. *Precautions to be observed in examining for the second division of the Second Group.*—If the solution has become very dilute during the course of the analysis, it will render the detection of the Mg more certain, if, before adding the  $\text{Na}_2\text{HPO}_4$ , the solution is concentrated. In any case, time must be allowed for the formation of the precipitate, the solution must be quite cold when the reagent is added, and after the addition of the reagent the solution must be frequently shaken; as  $\text{MgNH}_4\text{PO}_4$  is more insoluble in water containing  $\text{NH}_4\text{HO}$  than in pure water, it is necessary to have  $\text{NH}_4\text{HO}$  in excess.

391. Frequently a flocculent precipitate is obtained on the addition of  $\text{Na}_2\text{HPO}_4$ , which is not due to the presence of Mg; Bloxam states that it is aluminic phosphate, but I have found that it is sometimes due to calcic phosphate arising from the lime in the filter-paper.

392. Answers to the following exercises must be written out.

#### EXERCISES.

135. What are the characters of the solutions of salts of Mn, Cu, Pb,  $\text{Fe}''$ , and  $\text{Fe}'''$ ?

136. What are the characteristic reactions by which you would distinguish, by the blowpipe, ores of lead, bismuth, zinc, and antimony?

137. Express by means of equations the action of  $\text{HNO}_3$  of different strengths on Zn, Fe, Cu, Ag, Sn, and Hg respectively; also the action of  $\text{H}_2\text{SO}_4$  and HCl on these metals.

138. Separate, 1st, into groups, and 2dly, from each other, the following substances: Cu, Mn, Ba, Al, Cd,  $\text{NH}_4$ , Zn, K, and Ca; confirm the presence of each by means of a characteristic reagent.

139. Classify the following metals into those which (a) decompose water in cold, (b) at the boiling temperature, (c) at a red heat, and (d) not at all:—

Pt, K, Zn, Mg, Cu, Mn, Al, Ag, Fe.

140. A solution acid to test-paper gives an orange precipitate by the action of  $\text{H}_2\text{S}$ : what substances must be absent, what may the precipitate contain, and how would you examine it?

141. Classify the following oxides into those which (a) are reduced to the metallic state by heat alone, (b) are not reduced by heat alone, (c) are not reduced by charcoal alone, (d) are reduced by charcoal, (e) are reduced by H, (f) are not reduced by H, (g) are reduced by CO:—

$\text{Bi}_2\text{O}_3$ ,  $\text{PbO}_2$ ,  $\text{Fe}_3\text{O}_3$ ,  $\text{K}_2\text{O}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{As}_2\text{O}_5$ ,  $\text{MnO}$ ,  $\text{MgO}$ ,  
 $\text{An}_2\text{O}_3$ ,  $\text{FeO}$ ,  $\text{SnO}_2$ ,  $\text{BaO}$ ,  $\text{CoO}$ .

142. Do the sulphides of the 5th group experience any change when dissolved in a solution of KHO or NaHO?

## ACIDS.

393. The acids may be divided into two classes, the INORGANIC and the ORGANIC. All the organic acids contain carbon as a constituent, and they and their salts are decomposed by heat, the metals of the salts being left, when they are the alkaline or alkaline earth metals, in the state of carbonates; the decomposition of the organic acids or their salts by heat is also attended in the majority of cases with the separation of carbon.

394. Acids, both organic and inorganic, do not admit of that accurate classification into groups which is the case with bases, many of them being members of more than one group.

## INORGANIC ACIDS.\*

395. The special properties of each acid are first described; then their division into groups, with a description of the properties of each group of acids; and finally the processes to be followed in preparing the solutions for the examination of the inorganic acids, and the methods to be pursued in the examination.

396. The student must make the experiments given under the head of each acid, and then test the behavior of the acids with the group reagents; after he has made these experiments he passes over the organic acids and proceeds to the *examination of liquids*.

## BEHAVIOR OF THE ACIDS AND THEIR RADICALS WITH REAGENTS.

CHROMIC ACID,  $\text{H}_2\text{CrO}_4$ .

*Solution for the reactions,  $\text{K}_2\text{CrO}_4$  in water.*

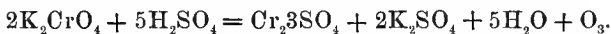
397. This acid has not been obtained in the solid state; it is supposed to exist in solution. CHROMIC ANHYDRIDE ( $\text{CrO}_3$ ) is a crystalline scarlet-colored solid, which deliquesces rapidly when exposed to the air; its solution possesses a deep reddish-brown tint.  $\text{CrO}_3$  may be obtained by adding undiluted  $\text{H}_2\text{SO}_4$  to a concentrated solution of  $\text{K}_2\text{Cr}_2\text{O}_7$ .  $\text{CrO}_3$  melts at  $190^\circ \text{C}$ .; at higher temperatures it is decomposed into  $\text{Cr}_2\text{O}_3$  and  $\text{O}$ .

398. There are *normal*, *acid*, and *basic chromates*. The normal salts of the alkalis, of Ca, Sr, Mg, Ni, Zn, and Cu, are soluble in water; the normal salts of the other metals are insoluble in  $\text{H}_2\text{O}$ , but they are nearly all soluble in  $\text{HNO}_3$ ; all the acid chromates are soluble in water. There are two acid chromates of potash, viz. the bichromate  $\text{K}_2\text{CrO}_4$ ,  $\text{CrO}_3$  or  $\text{K}_2\text{Cr}_2\text{O}_7$ , and the terchromate  $\text{K}_3\text{CrO}_4$ ,  $2\text{CrO}_3$  or  $\text{K}_2\text{Cr}_3\text{O}_{10}$ . The normal chromates of the alkalis and alkaline earths are *yellow*, the bichromates are *red*. The chromates of the heavy metals are *bright yellow*, *red*, or *brown*; the aqueous solutions of the soluble salts are the same color as the salts themselves; the *yellow* of the solution of a normal chromate changes, on the addition of an acid, to *red*, owing to the formation of an acid chromate.

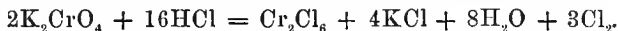
\* Oxalic acid, although an organic acid, has, on account of its frequent occurrence, been treated along with the inorganic acids.

The solution of the normal chromates of the alkalis are *alkaline*, and the bichromates are *acid*, to test-paper. Alkaline chromates may be prepared from insoluble chromates by fusing the latter in conjunction with alkaline carbonates or nitrates.

399. The normal alkaline chromates are not decomposed even at a full red heat. The normal chromates of the weaker bases are decomposed by heat, the  $\text{CrO}_3$  being decomposed into  $\text{Cr}_2\text{O}_3$  and  $\text{O}$ ; the acid chromates of the alkalis are decomposed by heat, a mixture of normal chromate and  $\text{Cr}_2\text{O}_3$  being left, and  $\text{O}$  given off. All the chromates are decomposed on being heated with undiluted  $\text{H}_2\text{SO}_4$ ; chromic sulphate and another sulphate being formed and  $\text{O}$  given off, thus:—



They are also decomposed on being heated with  $\text{HCl}$ , chromic chloride and another chloride being formed and  $\text{Cl}$  evolved, thus:—



$\text{CrO}_3$  and the chromates are also decomposed by  $\text{H}_2\text{S}$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{H}_2\text{O}$  being formed and  $\text{S}$  set free; they are reduced by  $\text{SO}_2$ , and also on being heated with  $\text{H}_2\text{T}$ ,  $\text{H}_2\text{O}$ , and by many other substances; on account of the facility with which  $\text{CrO}_3$  is reduced to  $\text{Cr}_2\text{O}_3$ , it possesses considerable oxidizing power. All these reactions are characterized by the change of color, of the solution from a *red* or *yellow* to *green*. As  $\text{H}_2\text{S}$  converts  $\text{CrO}_3$  into  $\text{Cr}_2\text{O}_3$ , we always obtain the  $\text{CrO}_3$  in the form of  $\text{Cr}_2\text{O}_3$  in testing for the bases.

400. If a very dilute acid solution of hydric peroxide ( $\text{H}_2\text{O}_2$ )\* is covered with a layer of ether, and a fluid containing chromic acid is added, the solution of  $\text{H}_2\text{O}_2$  acquires a fine blue color. By inverting the test-tube, closed with the thumb, repeatedly, without much shaking, the solution becomes colorless, whilst the ether acquires a blue color. The latter reaction is particularly characteristic. One part of potassic chromate in 40,000 parts of water suffices to produce it distinctly; the presence of vanadic acid mate-

\* Solution of  $\text{H}_2\text{O}_2$  may be easily prepared by triturating a fragment of baric peroxide ( $\text{BaO}_2$ ), about the size of a pea, with some water, and then adding a little dilute  $\text{HCl}$ . The solution keeps a long time without suffering decomposition. In default of  $\text{BaO}_2$ , impure  $\text{Na}_2\text{O}_2$  may be used instead, which is obtained by heating a fragment of  $\text{Na}$  in a small porcelain dish until it takes fire, and letting it burn.

rially impairs the delicacy of the test. After some time reduction of the  $\text{CrO}_3$  to  $\text{Cr}_2\text{O}_3$  takes place, and at the same time decoloration of the ether.—*Fresenius*.

### SULPHURIC ACID, $\text{H}_2\text{SO}_4$ .

*Solution for the reactions,  $\text{Na}_2\text{SO}_4$  in water.*

401.  $\text{H}_2\text{SO}_4$  is a heavy, colorless fluid, of an oily appearance, which possesses a strong affinity for  $\text{H}_2\text{O}$ , producing when mixed with it a great degree of heat. Its affinity for  $\text{H}_2\text{O}$  is so great, that it decomposes organic substances when placed in contact with them, removing their H and O, whilst the C is left behind as a black, coaly mass, a portion of which dissolves in the acid and communicates to it a brown tint. If heat is applied, the C is oxidized at the expense of the acid,  $\text{CO}_2$  and  $\text{SO}_2$  being formed; these facts may be illustrated by pouring some strong acid upon white sugar.  $\text{H}_2\text{SO}_4$ , at temperatures below its boiling-point ( $327^\circ\text{C}$ .), displaces all other acids from their combinations with bases, but above that temperature it is itself displaced by the non-volatile acids. SULPHURIC ANHYDRIDE ( $\text{SO}_3$ ) is a white solid, similar in appearance to asbestos. It evaporates and emits dense fumes on exposure to air. Its affinity for  $\text{H}_2\text{O}$  is so great, that it hisses like red-hot iron when brought in contact with it.

402. As  $\text{H}_2\text{SO}_4$  is bibasic, it forms with monatomic metals two classes of salts, viz. *neutral* salts,  $\text{M}_2\text{SO}_4$ , and *acid* salts,  $\text{MHSO}_4$ . The solutions of the neutral sulphates of the alkalies, of Ca, Mg, Mn, and Ag are *neutral* to test-paper; the neutral sulphates of the other bases and the acid sulphates of the alkalies are *acid* to test-paper.  $\text{BaSO}_4$ ,  $\text{PbSO}_4$  are *insoluble*,  $\text{SrSO}_4$ ,  $\text{CaSO}_4$  are *nearly insoluble*, all the other sulphates are insoluble, in water. Neither  $\text{PbSO}_4$  nor the sulphates of the metals of the alkalies and alkaline earths are decomposed when heated to redness, except  $\text{MgSO}_4$ , which loses its acid partially. The sulphates of Zn, Cd, Ni, Co, Cu, and Ag require an intense heat to decompose them; but the other sulphates part with their acid without difficulty when strongly ignited. All the sulphates, on being mixed with charcoal and heated, are decomposed; the sulphates of the metals of the alkalies and alkaline earths, and lead are reduced to sulphides. The other sulphates evolve  $\text{SO}_2$ , which may be detected by the smell, and by its bleaching moist Brazil-wood paper.

403. Sulphates in dilute solutions containing organic

matter are gradually converted into sulphides. Water containing a sulphate may therefore, after it has been kept a long time in a bottle or any closed vessel, be found to contain  $\text{H}_2\text{S}$ , although originally it was perfectly free from it.

404.  $\text{BaSO}_4$  is distinguished from all other baric salts, but baric selenate and baric fluosilicate, by *its insolubility in dilute acids*. Any *soluble baric salt* is therefore the best and most delicate test for  $\text{H}_2\text{SO}_4$ , whether free or combined, the solution being acidified with dilute  $\text{HCl}$  or dilute  $\text{HNO}_3$  before adding the baric salt.

405. Insoluble sulphates are completely decomposed by fusion with *alkaline carbonates*, an ALKALINE SULPHATE being produced along with a CARBONATE or an OXIDE of the other METAL.

406. When a sulphate, mixed with C and  $\text{Na}_2\text{CO}_3$  is fused upon a charcoal support by the inner blowpipe flame,  $\text{Na}_2\text{S}$  is produced. If the fused mass, moistened with water, be placed upon a piece of silver, a brown stain of  $\text{Ag}_2\text{S}$  will be formed.

407. "To detect free  $\text{H}_2\text{SO}_4$  in presence of a sulphate, the fluid under examination is mixed with a very little cane-sugar, and the mixture evaporated to dryness in a porcelain dish at  $100^\circ \text{C}$ . If free  $\text{H}_2\text{SO}_4$  was present a black residue remains, or, in the case of most minute quantities, a blackish-green residue. Other acids do not decompose cane-sugar in this way."

### SULPHUROUS ACID, $\text{H}_2\text{SO}_3$ .

408. This acid is formed when  $\text{SO}_2$  is passed into water; it attracts oxygen from the air, and becomes converted into  $\text{H}_2\text{SO}_4$ . Sulphurous anhydride ( $\text{SO}_2$ ) is a colorless gas. The acid and the anhydride have the odor of burning sulphur; they act as powerful reducing agents; they redden litmus paper and blanch Brazil-wood paper. The sulphites are decomposed by nearly all acids, save carbonic and boracic acids, with the liberation of sulphurous acid.

409.  $\text{BaCl}_2$  and  $\text{CaCl}_2$  produce white precipitates in solutions of the sulphides soluble in  $\text{HCl}$ .

410.  $\text{AgNO}_3$  produces a white precipitate in solutions of sulphides of  $\text{Ag}_2\text{SO}_3$ , which decomposes on the application of heat, becoming black:  

$$\text{Ag}_2\text{SO}_3 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + \text{Ag}_2$$

411. The smallest trace of  $\text{SO}_2$  in a gaseous mixture or of free  $\text{H}_2\text{SO}_3$  may be detected by means of strips of paper steeped in starch-paste, to which a small quantity of iodic acid or potassic iodate has been added. The iodic acid is reduced, and the iodine set free, which forms with the starch the well-known blue compound.

412. Sulphites when mixed with HCl and  $\text{SnCl}_2$  produce a yellowish precipitate,  $\text{SnS}_2$ ; sulphites treated with Zn and HCl evolve  $\text{H}_2\text{S}$ .

413.  $\text{H}_2\text{S}$  produces in solutions of  $\text{H}_2\text{SO}_3$  a white precipitate of S, whilst in solution there remains pentathionic acid ( $\text{H}_2\text{S}_5\text{O}_6$ ).

### HYPOSULPHUROUS OR TRIOSULPHURIC ACID, $\text{H}_2\text{S}_2\text{O}_3$ .

414. This acid is scarcely known in its free state; it is generally considered to be almost immediately resolved into  $\text{H}_2\text{SO}_3$  and S; but, according to Rose, it is comparatively stable in dilute solutions.

415. Solutions of hyposulphites give with *mercuric*, *plumbic*, and *argentic* salts white precipitates, which speedily become *yellow*, *brown*, and *black*.

416. Hyposulphites treated with HCl give off  $\text{SO}_2$  and S, which in this case is yellow, not white. When the hyposulphites are treated with iodine an iodide and a tetrathionate are formed:  $2\text{BaS}_2\text{O}_3 + \text{I}_2 = \text{BaI}_2 + \text{Ba}_4\text{S}_4\text{O}_{10}$ . These two reactions distinguish  $\text{H}_2\text{S}_2\text{O}_3$  from  $\text{H}_2\text{SO}_3$ .

### BORACIC ACID OR ORTHOBORACIC ACID, $\text{H}_3\text{BO}_3$ .

*Solution of Borax,  $2\text{NaBO}_2$ ,  $\text{B}_2\text{O}_3$ , in water.*

417. This acid is best obtained on the small scale by adding to a boiling concentrated solution of borax concentrated  $\text{H}_2\text{SO}_4$  or HCl until the liquid strongly reddens litmus; on cooling, the greater part of the acid separates from the solution in pearly looking scales, and on evaporating the mother-liquor another crop is obtained. The crystals retain a portion of the HCl or  $\text{H}_2\text{SO}_4$ ; from the former they are freed by gentle heating and recrystallization, but to free them from the latter acid they must be fused in a platinum crucible, and the fused mass crystallized.  $\text{H}_3\text{BO}_3$  is sparingly soluble in cold water, but is dissolved by three times its weight of boiling water; its aqueous solution turns blue litmus-paper, not bright red, like other acids, but of a claret color, and if the solution is allowed to evaporate on turmeric paper it turns the paper brown like the alkalies. It is soluble in alcohol, and the solution burns with a beautiful green-edged flame; this green color is not produced if the acid is in combination with a base. On evaporating an alcoholic or aqueous solution of the acid, a portion of it volatilizes with the vapor of the liquid, although it is not itself volatilized by heat. It decomposes solutions of the carbonates in the cold, but a brisk current of  $\text{CO}_2$  or  $\text{H}_2\text{S}$  passed through a concentrated solution will cause a separation of boracic acid in crystals. At a temperature of  $100^\circ\text{C}$ . it is converted into meta- or monobasic boracic acid,  $\text{HBO}_2$ , thus:—





At a red heat it is converted into *boracic anhydride*,  $B_2O_3$ , which is a brittle glassy solid; it volatilizes very slowly, even on intense ignition; at high temperatures it expels from salts all anhydrides more volatile than itself. It dissolves readily in water, forming  $H_3BO_3$ .

418.  $H_3BO_3$  is met with in its free state in many volcanic districts, especially in Tuscany, where it issues from the earth with the vapor of water. It is obtained in the form of crude borax, or tincal, from the salt lakes of India, Thibet, etc. "The borates are chiefly of two classes, namely, orthoborates (such as the normal trisodic borate,  $Na_3BO_3$ , and the penta-hydro-potassic diborate,  $KH_5B_2O_7$ ), and metaborates (such as the potassic metaborate,  $KBO_2$ )."

The borates are not decomposed on ignition, they are colorless, and they all, even the salts that contain an excess of acid, manifest alkaline reaction with test-paper. They are all, with the exception of the alkali salts, almost totally insoluble in water, but they dissolve readily in acids and in water containing ammoniac salts.

419. To detect a borate, add to the powdered substance under examination *strong*  $H_2SO_4$  and *alcohol* or *wood naphtha*; ignite the mixture subsequently. If a borate be present the borders of the flame will appear *green*, which becomes more distinct upon stirring, and the delicacy is further increased by repeatedly extinguishing and rekindling the flame. Copper salts impart the same color to the flame; Cu, if present, ought to be precipitated by  $H_2S$ , before testing for  $H_3BO_3$ . Chlorides interfere also with the test.

420. If a solution of an alkaline borate is mixed with HCl to slight but distinct acid reaction, and a slip of *turmeric* paper is half dipped into it, and then dried at  $100^\circ$  C., the dipped half shows a peculiar red tint; this reaction is very delicate. Care must be taken not to confound this coloration with the blackish-brown which turmeric paper acquires when moistened with strong HCl and dried, nor with the brownish-red which  $Fe_2Cl_6$  imparts to turmeric paper. By moistening turmeric paper reddened by  $H_3BO_3$  with a solution of an alkali, the color is changed to bluish-black or greenish-black; the addition of a little HCl restores the brownish-red color.—*Fresenius*.

421. To detect the boracic oxide, reduce the substance to be examined for it to a very fine powder, and then mix thoroughly with it five parts of  $KHSO_4$  and one part of  $CaF_2$ , and fuse the mass by the blowpipe flame in the loop of the

platinum wire; boric fluoride,  $\text{BF}_3$ , escapes and tinges the flame green for a few seconds.

### PHOSPHORIC ACID OR ORTHOPHOSPHORIC ACID, $\text{H}_3\text{PO}_4$ .

*Solution of common sodic phosphate,  $\text{Na}_2\text{HPO}_4$ , in water.*

422.  $\text{H}_3\text{PO}_4$  may be obtained in the form of colorless crystals; they deliquesce rapidly in the air. The aqueous solution of  $\text{H}_3\text{PO}_4$  has a strong acid reaction, and at a boiling heat expels most volatile acids from their combinations with bases. The aqueous solution may be heated to  $160^\circ \text{C}$ . without altering the character of the acid, but at  $215^\circ$  it is converted into the pyro-phosphoric acid,  $\text{H}_2\text{P}_2\text{O}_7$ , while above this temperature metaphosphoric acid,  $\text{HPO}_3$ , begins to be formed, and, after the application of a full red heat, constitutes the entire residue. PHOSPHORIC ANHYDRIDE,  $\text{P}_2\text{O}_5$ , is obtained by burning P in dry O or dry air; it appears under the form of white flakes, which rapidly absorb moisture from the air. It is a powerful dehydrating agent. It forms, by contact with water,  $\text{HPO}_3$ , but if boiled with the water  $\text{H}_3\text{PO}_4$ . After the  $\text{P}_2\text{O}_5$  has once been dissolved it cannot be converted back into the anhydride by heat.

423. The following are the general formulæ for the phosphates:  $\text{M}'\text{H}_2\text{PO}_4$ ; this class is frequently designated acid phosphates.  $\text{M}'_2\text{HPO}_4$ ,  $\text{M}''\text{HPO}_4$ ; these are frequently termed neutral phosphates.  $\text{M}_3\text{PO}_4$ ,  $\text{M}'''\text{MPO}_4$ ,  $\text{M}'''\text{PO}'_4$ ,  $\text{M}''_3(\text{PO}_4)_2$ , these are termed tribasic phosphates, there are in addition basic phosphate.  $\text{Na}_3\text{PO}_4$  and  $\text{K}_3\text{PO}_4$  are soluble in water, their solutions are alkaline, and they are decomposed by  $\text{CO}_2$ , thus:  $\text{Na}_3\text{PO}_4 + \text{CO}_2 + \text{H}_2\text{O} = \text{Na}_2\text{HPO}_4 + \text{NaHCO}_3$ .  $\text{Na}_2\text{HPO}_4$  and  $\text{K}_2\text{HPO}_4$  are soluble in water; their solutions have a feebly alkaline reaction.  $\text{NaH}_2\text{PO}_4$ ,  $\text{KH}_2\text{PO}_4$  are soluble in water; their solutions are strongly acid. The phosphates, with the exception of the alkaline ones, are nearly all insoluble in water.

424.  $\text{MgSO}_4$  or any soluble magnesian salt, produces in aqueous solutions of the phosphates, if concentrated, a white precipitate of  $\text{MgHPO}_4$ . A salt much more insoluble in water is produced by adding  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{HO}$ , and then  $\text{MgSO}_4$ ; the precipitate produced in this case is  $\text{MgNH}_4\text{PO}_4$ , which is slightly soluble in pure water, but almost insoluble in water containing  $\text{NH}_4\text{HO}$ . In dilute solutions it only appears after much agitation and the lapse of some time; agitation promotes its formation in all cases. This

test can only be applied when the *phosphates* are soluble in *ammonic* solutions.

425. Plumbic acetate produces a white precipitate of  $\text{Pb}_3(\text{PO}_4)_2$  soluble in  $\text{HNO}_3$ . If this precipitate after being dried is heated in the outer flame of the blowpipe, it becomes distinctly crystalline on cooling. This test is very characteristic, not only on account of the crystalline structure of the bead, but also from the circumstance that the  $\text{Pb}_3(\text{PO}_4)_2$  is the only lead salt which is not reduced to the metallic state when heated in the inner blowpipe flame. It is evident that, to render this test of any value, the  $\text{Pb}_3(\text{PO}_4)_2$  must be freed thoroughly, by washing, from all lead acetate.

426.  $\text{AgNO}_3$  throws down from solutions of phosphates containing one, two, or three atoms of fixed base, a light *yellow* precipitate of  $\text{Ag}_3\text{PO}_4$ , readily soluble in  $\text{HNO}_3$  and in  $\text{NH}_4\text{HO}$ . If the solution contained a phosphate containing three atoms of fixed base, after the precipitation the solution will be *neutral* to test-paper, but *acid* if the phosphate contains one or two atoms of fixed base, on account of the  $\text{HNO}_3$  that will be set free.

427. If to an acid solution of a phosphate containing the least possible excess of  $\text{HCl}$  or  $\text{HNO}_3$  a tolerably large amount of sodic acetate is added, and then a drop of  $\text{Fe}_2\text{Cl}_6$ , a *yellowish-white* gelatinous precipitate of  $\text{Fe}''' \text{PO}_4$  will be formed. An excess of  $\text{Fe}_2\text{Cl}_6$  must be avoided, as ferric acetate would thereby be formed, in which  $\text{Fe}''' \text{PO}_4$  is not insoluble. By this reaction the acid can be detected when combined with the alkaline earths, but it can only be held to be decisive in the absence of  $\text{H}_3\text{AsO}_4$ , as this acid forms a similar precipitate. To effect the complete separation of the acid from the alkaline earths,  $\text{Fe}_2\text{Cl}_6$  is added until the solution begins to be of a reddish color; it is then boiled, when the whole of the  $\text{Fe}$  is precipitated, partly as phosphate, partly as basic acetate. It must be filtered whilst hot; the filtrate contains the alkaline earths as chlorides. To detect by means of this reaction the acid in the presence of much  $\text{Fe}_2\text{O}_3$ , the  $\text{HCl}$  solution must be boiled with  $\text{NaHSO}_3$  until the  $\text{Fe}_2\text{Cl}_6$  is reduced to  $\text{FeCl}_2$ , which is indicated by the decoloration of the solution; add then  $\text{Na}_2\text{CO}_3$  until the fluid is nearly neutral, afterwards sodic acetate, and finally one drop of  $\text{Fe}_2\text{Cl}_6$ . The reason for this proceeding is that  $\text{Fe}'' 2\bar{\text{A}}$  does not dissolve  $\text{Fe}''' \text{PO}_4$ .

428. The solution of ammonic molybdate in  $\text{HNO}_3$  pro-

duces, immediately, in neutral or acid solutions of phosphates in the cold, a finely divided *yellow* precipitate, unless the quantity of phosphate is very minute; in that case the precipitate appears only after some hours, and the solution ought to be gently warmed. The precipitate is soluble in  $\text{H}_3\text{PO}_4$  and other acids, but it is rendered insoluble in them by an excess of the reagent; an excess of the fluid containing the phosphates must, therefore, be avoided. By this method  $\text{PO}_4$  can be separated from the metals of the alkaline earths, from Fe, Al, and other metals whose phosphates are insoluble in water. Presence of  $\text{H}_2\text{T}$  and other organic substances, and of large quantities of  $\text{HCl}$ , interferes with the precipitation. The precipitate is soluble in  $\text{NH}_4\text{HO}$ , and may, after it has been washed with the molybdic solution, be dissolved in it, and the  $\text{PO}_4$  precipitated from the solution by adding  $\text{NH}_4\text{Cl}$  and  $\text{MgSO}_4$ .  $\text{H}_3\text{AsO}_4$  gives no precipitate in the cold with the molybdic solution, but a yellow precipitate is formed if the solution be heated.  $\text{H}_4\text{SiO}_4$  gives no reaction in the cold with molybdic reagents, and only a yellow coloration, but no precipitate, after heating the solution. The production of a mere yellow coloration is, by the molybdic reagent, therefore, no indication of phosphoric acid.

429. The properties of the phosphates of Fe, Cr, Al, and of metals of the alkaline earths, and other methods for detecting  $\text{PO}_4$ , are given in pars. 183, 184, 185, 186, 187, and 188.

430. As arsenic acid gives precipitates with  $\text{MgSO}_4$ , with ferric salts and with molybdic acid similar to those given by phosphoric acid, the arsenic acid, when present, must be removed, either by reducing it by  $\text{SO}_2$  or by  $\text{H}_2\text{S}$ .

431. P may easily be detected in its compounds, even when they are mixed with large quantities of other substances, as follows:—

(a) The sample, having been ignited, is rubbed fine on the porcelain plate (see fig 3 in Plate), and is then introduced into a small glass tube of the thickness of a straw; into this tube, which is closed at the bottom, a piece of magnesium wire, about one-fourth of an inch in length, is placed so that it is covered by the powder. On heating the tube, magnesian phosphide is formed with incandescence. The black contents of the tube powdered on the plate give, on moistening with  $\text{H}_2\text{O}$ , the highly characteristic smell of  $\text{H}_3\text{P}$ . A piece of Na can be equally well used if the Mg wire cannot be procured.

(b) If it has been ascertained that the sample does not yield any film on porcelain in the upper oxidizing flame, the phosphates may be recognized by heating on platinum with borax and a thin piece of iron wire in the hottest part of the reducing flame, when a bright molten bead of iron phosphide is obtained, which can be extracted with the magnetized knife on crushing the bead under paper.—*Bunsen*.

### PYROPHOSPHORIC ACID, $\text{H}_4\text{P}_2\text{O}_7$ .

432. This acid may be obtained by exposing orthophosphoric acid to a temperature of  $215^\circ\text{C}$ . ; it appears under the form of a soft glass ; it is converted into orthophosphoric acid by boiling it in water, and it is converted into metaphosphoric acid when heated to redness. The acid is also converted into orthophosphoric acid on boiling solutions of its salts with strong acids.

433. The free acid does not give precipitates with  $\text{BaCl}_2$  and  $\text{AgNO}_3$ , but its salts give white precipitates with them.

434. White of egg is not precipitated by a solution of the acid, nor by solutions of its salts mixed with acetic acid. Ammonic molybdate, with addition of  $\text{NH}_4\text{HO}$ , fails to produce a precipitate.

### METAPHOSPHORIC ACID, $\text{HPO}_3$ .

435. This acid is obtained by acting on  $\text{P}_2\text{O}_5$  with cold water, or by heating  $\text{H}_4\text{P}_2\text{O}_7$  or  $\text{H}_3\text{PO}_4$  to redness ; it forms a transparent, colorless, glassy, uncrystallizable mass.

436. The solution of the acid gives precipitates with white of egg, with  $\text{AgNO}_3$  and  $\text{BaCl}_2$ . It gives no precipitate or coloration with ammonic molybdate.

437. The metaphosphates do not coagulate the albumen of white of egg unless acetic acid be added, which liberates  $\text{HPO}_3$ . This is its most characteristic test.

438. This acid is converted slowly at ordinary temperatures, quickly at the boiling heat, into  $\text{H}_3\text{PO}_4$ .

### CARBONIC ACID, $\text{H}_2\text{CO}_3$ .

*Solution for the reactions,  $\text{Na}_2\text{CO}_3$  in water.*

439.  $\text{H}_2\text{CO}_3$  is supposed to be formed when  $\text{CO}_2$  is passed into  $\text{H}_2\text{O}$ , but it has never been obtained; if it exists it decomposes when its solution is evaporated. CARBONIC ANHYDRIDE,  $\text{CO}_2$ , exists at the common temperature and pressure as a colorless, inodorous, and non-inflammable gas. Being heavier than the atmosphere in the proportion of 1.5 to 1, it can be decanted from one vessel to another like a liquid. It reddens blue litmus paper previously

moistened with water, which after a time returns to its original color, owing to the  $\text{CO}_2$  having volatilized. It is soluble in cold water, but when the solution is heated it escapes.

440. As  $\text{H}_2\text{CO}_3$  is bibasic, it forms with the monatomic metals two classes of salts, viz., neutral or normal salts,  $\text{M}'_2\text{CO}_3$ , and acid salts,  $\text{M}'\text{HCO}_3$ ; the neutral and acid salts of the metals of the alkalies are alkaline to test-paper. The neutral alkaline carbonates are the only *neutral* salts of this acid which are soluble in water. The carbonates are decomposed by all free acids soluble in water ( $\text{HCy}$  and  $\text{H}_2\text{S}$  excepted), with evolution of  $\text{CO}_2$ .

441. To detect  $\text{CO}_2$ , add to the solution or solid substance under examination  $\text{HCl}$ , and warm the solution, if sufficient gas for detection cannot be procured without. Should any gas be evolved, allow it to accumulate by placing the thumb on the mouth of the test-tube, and afterwards decant it (taking care not to allow any of the liquid to pass over along with it) into another test-tube half filled with *lime-water*. A white precipitate of  $\text{CaCO}_3$  will be produced if  $\text{CO}_2$  is present.

442. When the solution under examination contains only a minute quantity of a carbonate, it is sometimes a matter of difficulty, especially to young students, to decant the  $\text{CO}_2$  into the test-tube containing the lime-water; this is especially the case if the solution contains  $\text{Na}_2\text{HPO}_4$ , as  $\text{CO}_2$  is very soluble in a solution of that salt. In such cases it would be better first to precipitate the  $\text{CO}_3$  in conjunction with  $\text{CaO}$  or  $\text{BaO}$ , by adding to the solution under examination a solution of  $\text{CaCl}_2$  or  $\text{BaCl}_2$ , collecting the precipitate produced upon a filter, and after all the fluid has filtered off to transfer the precipitate again to the test-tube, moisten with water, then add  $\text{HCl}$ , and if any effervescence takes place to collect the gas in lime-water in the manner just described (441).

443.  $\text{CaCl}_2$  and  $\text{BaCl}_2$  produce in solutions of the neutral alkaline carbonates an *immediate* precipitate of  $\text{CaCO}_3$  or of  $\text{BaCO}_3$ ; but these chlorides in dilute solutions of the acid carbonates ( $\text{M}'\text{HCO}_3$ ) form precipitates only after *ebullition*; in solutions of the free acid these reagents produce no precipitates.

444. Many of the insoluble carbonates dissolve in water containing  $\text{CO}_2$ , from which solutions they are precipitated on boiling, because the  $\text{CO}_2$  is expelled. It is in this state that most of the  $\text{Ca}$  and  $\text{Mg}$  in spring and river

water exists. The incrustations which are formed in the vessels in which such waters are boiled are due to the precipitation of these carbonates occasioned by the expulsion of the  $\text{CO}_2$ . The  $\text{CO}_2$  in waters is best detected by adding to them *lime-water*; by this means not only is the  $\text{CaCO}_3$  which is formed precipitated, but also that which pre-existed in the solution. This process is employed on the large scale for softening hard waters (waters containing in solution calcic and magnesian salts.) It is called, after the inventor, Clark's process.

445. All the carbonates, with the exception of those of the alkalies, lose their acid upon ignition, the metal being left either in an oxidized or uncombined state, according to its greater or less affinity for oxygen.

446. *The following precautions must be attended to in testing for this acid:* When the substance is in the solid state it should be reduced to fine powder, and a little water should be added prior to the acid, to displace the air in its pores, otherwise an apparent effervescence will ensue from the expulsion of air. In the case of alkaline carbonates the decomposing acid must be added until the solution reddens blue litmus paper—that is, until the acid is in *excess*; otherwise the carbonic acid set free may combine with some of the undecomposed carbonate, forming with it an acid carbonate, no effervescence consequently taking place. No decomposition takes place on the addition of strong  $\text{HNO}_3$  to  $\text{BaCO}_3$ , especially the native carbonate, because  $\text{Ba}(\text{NO}_3)_2$  is insoluble in the strong acid. Water must therefore be added, as well as the acid, for the decomposition to be effected in this and many other cases.

#### OXALIC ACID, $\text{H}_2\text{C}_2\text{O}_4 = \text{H}_2\bar{\text{O}}$ .

*Solution for the reactions,  $(\text{NH}_4)_2\bar{\text{O}}$  in water.*

447.  $\text{H}_2\bar{\text{O}}$  crystallizes from its aqueous solutions in four-sided prisms, which contain 2 ats. of water. The acid is very soluble in water and alcohol; its solution is very acid and poisonous. The crystallized acid melts at about  $98^\circ$  C. in its water of crystallization. The dry acid sublimes at  $165^\circ$  in slender white needles; part of it is, however, decomposed, and larger portions of it at an increased temperature, into  $\text{CO}_2$  and formic acid,  $\text{HCHO}_2$ , the latter being resolved into carbonic oxide,  $\text{CO}$ , and  $\text{H}_2\text{O}$ . Heated with an excess of alkali, a carbonate is formed and  $\text{H}$  evolved.  $\text{Cl}$  does not act on dry  $\text{H}_2\text{C}_2\text{O}_4$ , but in the presence

of moisture it quickly decomposes it, thus:  $\text{H}_2\text{C}_2\text{O}_4 + \text{Cl}_2 = 2\text{CO}_2 + 2\text{HCl}$ .  $\text{H}_2\text{O}$  may be crystallized from hot  $\text{HNO}_3$ , but by long-continued boiling in  $\text{HNO}_3$  it is slowly oxidized,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  being formed. OXALIC ANHYDRIDE,  $\text{C}_2\text{O}_3$ , has not been obtained. When  $\text{H}_2\text{C}_2\text{O}_4$  is dehydrated by concentrated  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ , or other dehydrating substances, the  $\text{C}_2\text{O}_3$  splits up at the same time into  $\text{CO}_2$  and  $\text{CO}$ .

448.  $\text{H}_2\text{C}_2\text{O}_4$ , like other bibasic acids, forms, with the monatomic metals, two classes of salts, viz. *neutral salts*,  $\text{M}'_2\text{C}_2\text{O}_4$ , and *acid salts*,  $\text{M}'\text{HC}_2\text{O}_4$ ; but it also forms a third group of super-acid salts,  $\text{KH}_2\text{C}_2\text{O}_4$ . The oxalates of the alkaline metals are soluble in water; the rest are almost all insoluble in water, but soluble in dilute acids. All the oxalates are decomposed by heat. The oxalates of the more easily reducible metals, as Ag, Hg, Cu, give off  $\text{CO}_2$ , the metal being left in the metallic state; the oxalates of the less reducible metals, whose carbonates are decomposed by heat, as Zn, Mg, etc., give off  $\text{CO}_2$  and  $\text{CO}$ , the metal being left as oxide. The oxalates of the metals whose carbonates are not decomposed by heat, as K and Na, or not easily decomposed, as Ba, Sr, and Ca, give off  $\text{CO}$ , the metal being left as carbonate.

449. The *acid* or *oxalates*, heated with concentrated  $\text{H}_2\text{SO}_4$ , give off, with effervescence,  $\text{CO}_2$  and  $\text{CO}$ , and if a light be applied to these gases as they issue from the mouth of the test-tube the  $\text{CO}$  will burn with a *blue* flame.

450. The *acid* or *oxalates*, on being mixed with some finely powdered  $\text{MnO}_2$  (which must be free from carbonates), a little  $\text{H}_2\text{O}$  added, and a few drops of concentrated  $\text{H}_2\text{SO}_4$ , considerable effervescence ensues, owing to the  $\text{CO}_2$  which is formed thus:  $\text{MnO}_2 + \text{K}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{SO}_4 = \text{Mn}''\text{SO}_4 + \text{K}_2\text{SO}_4 + 2\text{H}_2\text{O} + 2\text{CO}_2$ . This reaction is employed for estimating the amount of  $\text{MnO}_2$  in manganese ore (par. 127).

451. The soluble calcic salts and lime-water produce, even in highly dilute *solutions* of oxalates, a white precipitate of  $\text{CaO}$ , which is insoluble in acetic acid.

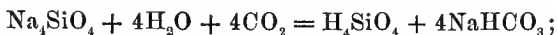
#### SILICIC ACID OR ORTHOSILICIC ACID, $\text{H}_4\text{SiO}_4$ .

452.  $\text{H}_4\text{SiO}_4$  may be obtained by passing silicic fluoride into water:—



it may also be obtained by passing  $\text{CO}_2$  into a solution of a soluble silicate:—





or by treating a solution of a soluble silicate with HCl. The  $\text{H}_4\text{SiO}_4$ , obtained in decomposing solutions of the alkaline silicates with acids, separates from the solutions in the form of a gelatinous mass, which is nearly insoluble in water and acids; but if a dilute solution of the silicate be poured into a considerable excess of HCl the  $\text{H}_4\text{SiO}_4$  remains in solution, but is precipitated on neutralizing the solution with an alkali. If the solution of the  $\text{H}_4\text{SiO}_4$  is placed in one of Graham's dialysers, and the water in the outer vessel is changed every twenty-four hours, in four or five days the alkaline chloride and the excess of HCl have diffused so completely that the liquid in the dialyser contains not even a trace of them, but is a pure solution of  $\text{H}_4\text{SiO}_4$ , containing about 5 per cent. of the acid; the solution may be concentrated in a flask until it contains 14 per cent. of the acid; this solution is tasteless, limpid, colorless, and feebly acid; in a few days it becomes converted into a solid, transparent, jelly-like mass, which shrinks and gives up water even in closed vessels; the coagulation is retarded by HCl and by small quantities of KHO or NaHO. By evaporating this pure solution of  $\text{H}_4\text{SiO}_4$  at  $15.5^\circ \text{C}$ ., in a vacuum, a transparent, glassy, very lustrous mass is left, which, after drying over  $\text{H}_2\text{SO}_4$ , yields **DIBASIC SILICIC ACID**,  $\text{H}_2\text{SiO}_3$ ; in addition to these two there is evidence of other silicic acids. **SILICIC ANHYDRIDE**,  $\text{SiO}_2$ , is obtained on igniting  $\text{H}_4\text{SiO}_4$  or  $\text{H}_2\text{SiO}_3$  as a gritty white powder; it occurs in nature in two forms, the crystalline and amorphous; *rock crystal*, *quartz*, *amethyst* (colored purple by ferric oxide) are pure, or nearly pure, crystallized  $\text{SiO}_2$ ; *agate* and *chalcedony* consist of a mixture of crystallized and amorphous  $\text{SiO}_2$ ; *opal* consists of the amorphous form with a varying quantity of water. Silica is the principal constituent of sandstones; it is also one of the constituents of felspar and of numerous other minerals. All the artificial forms of  $\text{SiO}_2$  are amorphous.  $\text{SiO}_2$ , whether natural or artificial, is insoluble in water and all acids except HF, and it requires for its fusion a heat as intense as that of the oxyhydrogen blowpipe; at that temperature it melts to a transparent glass and is amorphous.  $\text{H}_4\text{SiO}_4$  and amorphous  $\text{SiO}_2$  dissolve in hot aqueous solutions of the fixed and carbonated alkalies; but the crystalline  $\text{SiO}_2$  is dissolved by these reagents with far greater difficulty and in much less quantity, and it is also much more slowly

attacked by HF. The amorphous and crystallized  $\text{SiO}_2$ , on being fused with alkaline carbonates, are converted into alkaline silicates, which are decomposed by acids,  $\text{H}_2\text{SiO}_4$  separating. At common temperatures the silicic acids are weak acids, but at a red heat they expel  $\text{H}_2\text{SO}_4$  and the more volatile acids from their salts.

453. "The composition of the SILICATES presents many varieties; some correspond to  $\text{H}_4\text{SiO}_4$ , for example  $\text{Mg}''_2\text{SiO}_4$ ; others, such as  $\text{Na}_2\text{SiO}_3$ , correspond to the bibasic acid  $\text{H}_2\text{SiO}_3$ , and there are also the following among other silicates,  $\text{K}_2\text{Si}_2\text{O}_5$ ,  $\text{Na}_2\text{Si}_3\text{O}_7$ ,  $\text{Na}_2\text{Si}_4\text{O}_9$ ." The alkaline silicates are the only silicates soluble in water; their solutions are alkaline to test-paper, and they are decomposed in solution by all acids; on evaporating their solutions to dryness along with a slight excess of HCl or  $\text{HNO}_3$ , and igniting the residue for some little time and then treating it with dilute HCl or  $\text{HNO}_3$ , the other substances dissolve, whilst the whole of the  $\text{SiO}_2$  remains undissolved as a whitish gritty powder. On adding  $\text{NH}_4\text{Cl}$  to a concentrated solution of an alkaline silicate, a gelatinous precipitate separates.

454. Some of the silicates insoluble in  $\text{H}_2\text{O}$  are dissolved with decomposition by HCl or  $\text{HNO}_3$ ; some that are not decomposed by these acids are decomposed by concentrated  $\text{H}_2\text{SO}_4$ . The silicates which are not acted upon by any acids but HF are decomposed by fusion with the alkaline carbonates, and also with  $\text{BaH}_2\text{O}_2$ .

455. The silicates decomposable by HCl or  $\text{HNO}_3$  ought to be reduced to the finest powder, and be digested in the acid for some time at a gentle heat, with constant stirring, when the decomposition is effected; the mixture must be evaporated to dryness on the water-bath and the residue heated until acid fumes cease to be evolved; the dry mass is then moistened with HCl and heated with water, and then filtered; the filtrate must be examined for the bases and other acids, and the insoluble portion for  $\text{SiO}_2$ .

456. HF and  $\text{SiO}_2$  mutually decompose each other, gaseous  $\text{SiF}_4$  and  $\text{H}_2\text{O}$  being formed; silicates are converted by HF into silico-fluorides;  $\text{M}''\text{SiF}_6$  and these salts, on being heated with  $\text{H}_2\text{SO}_4$ , are converted into sulphates, HF and  $\text{SiF}_4$  being evolved. The silicates undecomposable by other acids are decomposed by HF, but the fusion process is better suited for qualitative purposes.

457. Silicates not decomposed by acids must be reduced to the finest powder, and then intimately mixed with a

mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$ , and the mixed mass fused in a platinum crucible until the evolution of  $\text{CO}_2$  ceases. The crucible, when cold, is put into an evaporating dish containing dilute  $\text{HCl}$ . When the fused mass is detached from the crucible, remove the crucible and evaporate the mixture to dryness, and ignite just in the same way as the solution in 455 is directed to be treated. The fixed alkalies cannot, of course, be sought for in that portion which has been fused with the alkaline carbonate; to ascertain whether they are present, another portion of the silicate must be fused with  $\text{BaH}_2\text{O}_2$ . For this purpose "mix one part of the very finely pulverized substance with four parts of  $\text{BaH}_2\text{O}_2$ ; expose the mixture for half an hour, in a platinum crucible, to strong heat, and then treat the fused or agglutinated mass with  $\text{HCl}$  and water until it is dissolved. Precipitate the Ba and all the bases in the silicate, with the exception of Mg and the alkalies, with  $\text{NO}_4\text{HO}$  and  $(\text{NH}_4)_2\text{CO}_3$ ; filter, evaporate to dryness, ignite, dissolve the residue in water, precipitate again with  $\text{NH}_4\text{HO}$  and  $(\text{NH}_4)_2\text{CO}_3$ , filter, evaporate, ignite;" then test for K and Na in the usual way.

458. When  $\text{SiO}_2$  or  $\text{H}_4\text{SiO}_4$  is fused with  $\text{Na}_2\text{CO}_3$  before the blowpipe, a transparent colorless bead is formed, the  $\text{CO}_2$  being expelled. A small quantity of  $\text{Na}_2\text{CO}_3$  ought only to be employed, as an opaque bead is produced when it is added in excess.

#### HYDROFLUORIC ACID, $\text{HF}$ .

459. This acid is best obtained by the action of concentrated  $\text{H}_2\text{SO}_4$  on  $\text{CaF}_2$ , fluor spar. The powdered mineral is gently heated with the acid in a retort of lead, and the  $\text{HF}$  condensed in a receiver of the same metal. It is obtained in the form of a very volatile liquid, strongly acid and corrosive, fuming in the air. It burns the skin like red-hot iron, causing a sore which is not easily healed. It is distinguished from all other acids by dissolving  $\text{SiO}_2$  and the silicates which are insoluble in the other acids; on this account it cannot be prepared or kept in glass vessels.

460. "If a finely pulverized fluoride, no matter whether soluble or insoluble, is heated in a platinum crucible with concentrated  $\text{H}_2\text{SO}_4$ , the crucible covered with the convex face of a watch-glass, coated on that side with beeswax, which has been removed again in some places by tracing

lines in it with some pointed instrument,\* the hollow of the glass filled with water, and the crucible gently heated for the space of half an hour or an hour, the exposed lines will, upon the removal of the wax, be found etched into the glass. If the quantity of HF disengaged by the  $\text{H}_2\text{SO}_4$  is very minute, the etching is often invisible upon the removal of the wax; it will, however, in such cases reappear when the plate is breathed upon. This appearance of the etched lines is owing to the unequal capacity of condensing water which the etched and the untouched parts of the plate respectively possess." This method cannot be adopted if the substance containing the F is not decomposed by  $\text{H}_2\text{SO}_4$ , or if *silicic* acid is present; the silicic acid must be got rid of, in the way to be described, before we can discover F.

461. If nascent HF meet with  $\text{SiO}_2$ , we have seen they are mutually decomposed (par. 456). Should the substance examined contain, therefore,  $\text{SiO}_2$  as well as F,  $\text{SiF}_4$ , and not HF, will be disengaged by the  $\text{H}_2\text{SO}_4$ .  $\text{SiF}_4$  in the pure state is a colorless gas, which has a suffocating acid smell, and which emits fumes in contact with the air; it reacts with water, and forms  $\text{H}_4\text{SiO}_4$ , which is deposited in the gelatinous state, and  $\text{H}_2\text{SiF}_6$ , hydrofluosilicic acid, which remains in solution.  $\text{SiF}_4$  does not attack glass; but the glass becomes covered, when damp, with a very adhesive coating of  $\text{H}_4\text{SiO}_4$ , which impairs its transparency, owing to the decomposition of the  $\text{H}_2\text{O}$  and  $\text{SiF}_4$ .  $\text{H}_2\text{SiF}_6$  combines with the metallic oxides, and forms with them a class of salts called silicofluorides, which are decomposed by excess of alkali,  $\text{SiO}_2$  being precipitated, and an alkaline fluoride remaining in solution.

462. To detect F in silicated fluorides which are *decomposable* by  $\text{H}_2\text{SO}_4$ , boil the substance with concentrated  $\text{H}_2\text{SO}_4$  in a flask, retort, or test-tube, to which is attached a bent tube; conduct the evolved  $\text{SiF}_4$  into a solution of  $\text{NH}_4\text{HO}$ ;  $\text{NH}_4\text{F}$  and  $\text{SiO}_2$  will be formed; heat, filter, evaporate in a platinum crucible to dryness, and examine the residue by the method described in 460. If the substance under examination contains only a slight

\* The coating with the wax may be readily effected by heating the glass cautiously, putting a bit of wax upon the convex face, and spreading the fused mass equally over it. The instrument used for tracing the exposed lines should not be too hard; a pointed piece of wood answers best. The removal of the wax coating is effected by heating the glass gently and wiping the wax off with a cloth.

trace of F and no other volatile acid, it is better to add a very little marble to the substance, so as to insure a continuous slight evolution of gas. When the  $\text{H}_2\text{SO}_4$  boils, all the  $\text{SiF}_4$  is given off.

463. "Compounds not decomposable by  $\text{H}_2\text{SO}_4$  must first be fused with four parts of  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$ . The fused mass is treated with water, the solution filtered, the filtrate concentrated by evaporation, allowed to cool, transferred to a platinum or silver vessel,  $\text{HCl}$  added to feebly acid reaction, and the fluid let stand until the  $\text{CO}_2$  has escaped. It is then supersaturated with  $\text{NH}_4\text{HO}$ , heated, filtered into a bottle,  $\text{CaCl}_2$  added to the still hot fluid, the bottle closed, and allowed to stand at rest. If a precipitate ( $\text{CaF}_2$ ) separates after some time, it is collected on a filter, dried, and examined by the method described in 460."—*H. Rose*.

464. If a fluoride mixed with  $\text{KHSO}_4$  is heated in a test-tube,  $\text{HF}$  is disengaged, which is easily detected by the etching of the glass. Consult also pars. 679 and 671, 9th b.

#### HYDROSULPHURIC ACID (*Sulphuretted Hydrogen*, $\text{H}_2\text{S}$ ).

465. This acid exists at the common temperature and pressure as a colorless inflammable gas, possessing a highly offensive odor, resembling that of rotten eggs. It burns with a blue flame, the products of combustion being  $\text{SO}_2$  and  $\text{H}_2\text{O}$ . It is soluble in water, three volumes of which dissolve one volume of the gas; this solution reddens litmus paper. On exposing the gas in a state of solution to the air, it is decomposed,  $\text{H}_2\text{O}$  being formed, and S being separated.

466. The sulphides of the metals of the alkalies and alkaline earths are the only metallic sulphides which are soluble in water; we have seen that these metals of the alkalies and alkaline earths form also sulph-hydrates and polysulphides, and these, as well as the monosulphides, are soluble in water, and their solutions are also alkaline to test-paper. The sulph-hydrates are distinguished from the sulphides by evolving  $\text{H}_2\text{S}$  on being decomposed by a metallic salt:  $2\text{KHS} + \text{MnSO}_4 = \text{K}_2\text{SO}_4 + \text{MnS} + \text{H}_2\text{S}$ ; and the polysulphides are distinguished from the sulphides and sulph-hydrates in that a separation of sulphur, as well as an evolution of  $\text{H}_2\text{S}$ , attends their decomposition by acids.

467. The color of the insoluble metallic sulphides and their behavior with acids and other reagents have been noticed in the basic groups.

468. The sulphides soluble in water and the sulphides which are decomposed by  $\text{HCl}$  evolve  $\text{H}_2\text{S}$  on being treated with  $\text{HCl}$ , which, from its characteristic smell, is easily recognized. When the quantity is so minute that the smell fails to afford a sufficient proof, it may be detected by holding a piece of paper moistened with a solution of any soluble LEAD SALT over the mouth of the test-tube, as a brown or black coating of  $\text{PbS}$  will be formed upon the paper. To detect a trace of an alkaline sulphide in the presence of a free alkali or alkaline carbonate, add to the solution a solution of  $\text{PbO}$  in  $\text{NaHO}$ , which may be prepared by adding to a solution of  $\text{PbA}_2$  one of  $\text{NaHO}$  until the solution which first forms is redissolved.

469. Sulphides which are not readily acted on by dilute  $\text{HCl}$  alone are readily acted on and evolve abundance of  $\text{H}_2\text{S}$  on the addition of a piece of  $\text{Zn}$ .

470. When sulphides are dissolved in  $\text{HNO}_3$  or aqua regia,  $\text{H}_2\text{SO}_4$  is formed along with a separation of  $\text{S}$ . In the case of sulphides, therefore, which, from their insolubility in  $\text{HCl}$ , must be dissolved in  $\text{HNO}_3$  or aqua regia, the sulphur is converted into  $\text{H}_2\text{SO}_4$ , and not given off as  $\text{H}_2\text{S}$ .

471. To ascertain whether the  $\text{S}$  existed in an unoxidized state, when  $\text{HNO}_3$  or aqua regia has been employed as the solvent of the substance under examination, a small portion of the *original* substance, in fine powder, must be fused with a little solid  $\text{KHO}$  or  $\text{NaHO}$ , in a platinum spoon, by means of the blowpipe flame. The fused mass must then be dissolved in a little water and filtered; a bright strip of silver (or polished coin) is put into the solution, and the fluid warmed. If a sulphide were present, a brownish-black film of  $\text{Ag}_2\text{S}$  will form upon the metal. This film may be removed afterwards by rubbing the metal with leather and  $\text{CaO}$ . For other methods of detecting sulphides, see pars. 671, 7th; 673, d; 675 and 678.

### HYDROCHLORIC ACID, $\text{HCl}$ .

*Solutions for the reactions,  $\text{NaCl}$  in water.*

472. This acid is a transparent and colorless gas, of a pungent, acrid, suffocating smell, and fuming strongly in moist air. It is absorbed in large proportion by water,

forming the common liquid  $\text{HCl}$ , which is a mere solution of the gas in water. With the exception of  $\text{AgCl}$  and  $\text{HgCl}$ , all the neutral metallic chlorides are soluble in water; the solutions of the chlorides of the metals, of the alkalis, and alkaline earths of  $\text{Mn}$  are neutral to test-paper.

473. When a chloride is heated with  $\text{MnO}_2$  and  $\text{H}_2\text{SO}_4$ ,  $\text{Cl}$  is evolved, which may be recognized by its odor and GREENISH-YELLOW COLOR.

474. When a chloride in the solid state and dry is heated with  $\text{K}_2\text{CrO}_4$  in the solid state and *concentrated*  $\text{H}_2\text{SO}_4$ , a brown gas is disengaged, which condenses into a blood-red liquid, CHLOROCHROMIC ACID,  $\text{CrO}_2\text{Cl}_2$ . On the addition of  $\text{NH}_4\text{HO}$  in excess the color changes to a yellow, owing to the formation of  $(\text{NH}_4)_2\text{CrO}_4$ ; upon the addition of an acid, the yellow changes to a reddish-yellow color, owing to the formation of  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ .

475. If in a bead of  $\text{NaNH}_4\text{HPO}_4$  on a platinum wire,  $\text{CuO}$  be dissolved in the outer blowpipe flame in sufficient quantity to make the mass nearly opaque, a trace of substance containing  $\text{Cl}$  added to it while still in fusion, and the bead then exposed to the reducing flame, a fine BLUE-COLORED flame, inclining to PURPLE, will be seen encircling it so long as  $\text{Cl}$  is present.—*Berzelius*.

476. Free  $\text{Cl}$  may be readily detected in a solution by adding some of the fluid to a solution containing a ferrous salt and a sulphocyanide; the solution turns red by reason of the  $\text{Cl}$  converting the ferrous into a ferric salt; it may also be detected in the absence of nitrous acid, by adding the solution to one of  $\text{KI}$  and starch paste, when a blue color will be instantly produced.

### HYDRIODIC ACID, $\text{HI}$ .

*Solution for the reactions,  $\text{KI}$  in water.*

477.  $\text{HI}$  and the iodides resemble in their properties the corresponding compounds of  $\text{Cl}$  and  $\text{Br}$ .  $\text{HI}$  is gaseous; it is extremely soluble in water, and the solution, which is colorless, resembles in properties that of  $\text{HCl}$  and  $\text{HBr}$ ; but it is more easily decomposed than the two latter compounds by substances which have an affinity for  $\text{H}$ , and also by those substances which have an affinity for the other constituent. The colorless solution turns speedily to a reddish-brown when in contact with the air, owing to the formation of  $\text{H}_2\text{O}$  and the liberation of  $\text{I}$ , which is dissolved by the undecomposed  $\text{HI}$ .  $\text{HI}$  and the iodides are

decomposed by Cl and Br, owing to these two elements having a greater affinity for H and the metals. HI, in the gaseous state, may be obtained by placing in a small retort 10 parts of KI with 5 of  $H_2O$  and 20 of I, then drop in cautiously 1 part of P in small pieces, and apply a gentle heat; the following equation explains the reaction:  $4KI + 5I_2 + P_2 + 8H_2O = 2K_2HPO_4 + 14HI$ . HI in solution is easily prepared by suspending I in water and passing  $H_2S$  through the mixture; HI is formed and S is set free. "The iodides, as a rule, are less volatile, more insoluble and more easily decomposed, than the chlorides and bromides. The iodides of Sn, Sb, and As, like the chlorides and bromides, are decomposed by  $H_2O$ . The hydrated iodides of Mg, Zn, and Al are, like the chlorides and bromides, decomposed by heat into metallic oxide and HI. In addition to the iodides of Pd, Pt, and Au, AgI, unlike the chloride and bromide of Ag, is decomposed at a red heat. All iodides, except those of the alkali- and alkaline-earth group, are decomposed at a red heat by a current of H. The iodides, with the exception of those last mentioned, and those of Pb and Bi, are also decomposed by O at a red heat."

478.  $HgNO_3$  throws down from solutions of the iodides a yellowish-green precipitate of  $HgI$ .

479.  $HgCl_2$  throws down a red precipitate of  $HgI$ , which is soluble in an excess of the  $HgCl_2$  or of KI.

480. Soluble lead salts precipitate an orange-yellow of  $PbI_2$ .

481. Free I forms with *starch*, even in highly dilute solutions, a compound of a deep *blue color*. If the I is in a state of combination with H or any metal, it is necessary to liberate it before applying the starch test; the blue compound is decolorized at a temperature of  $70^\circ$  or  $80^\circ$  C., but recovers its color as the liquid cools; it is decomposed by Cl, Br, and the alkalis.

482. Cl liberates I from its combinations; if added in excess, they combine, forming colorless  $ICl_3$ .

483. If iodides are heated with  $H_2SO_4$  and  $MnO_2$ , the I sublimes in the form of violet-colored vapors, which are easily recognized; this process is the one followed in the manufactory for obtaining the iodine from the kelp liquors.

484. Palladious chloride,  $PdCl_2$ , produces even in very dilute solutions of HI and of metallic iodides a brownish-black precipitate of  $PdI_2$ , which is insoluble or nearly so in cold dilute HCl and  $HNO_3$ .  $PdCl_2$  does not precipitate Br from its solutions.



485. Pure  $\text{HNO}_3$ , free from nitrous acid, decomposes HI or iodides only when acting upon them in its concentrated form, particularly when aided by the application of heat. But  $\text{HNO}_2$  and *peroxide of nitrogen*,  $\text{N}_2\text{O}_4$ , decompose HI and iodides with the greatest facility even in the most dilute solutions. Colorless solutions of iodides, therefore, acquire immediately a brownish-red color upon the addition of some red fuming  $\text{HNO}_3$ , or of a mixture of this with concentrated  $\text{H}_2\text{SO}_4$ , or, better still, upon addition of a solution of  $\text{N}_2\text{O}_4$  in  $\text{H}_2\text{SO}_4$ , or of nitrite of potash and some  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$ . From more concentrated solutions the I separates under these circumstances in the form of small black plates or scales, whilst nitric oxide gas,  $\text{NO}$ , and iodine vapor escape.

486. The best method of detecting I in a solution is to mix with the liquid a little starch paste, and acidify it with  $\text{HCl}$ . A solution of  $\text{KNO}_3$ \* is then to be added, when, if much I be present, a dark blue color will be instantly produced; if a very small quantity only—as, for instance, the two or three millionth part—then a few seconds elapse before the blue color makes its appearance.

487. When a solution containing 1 part of  $\text{CuSO}_4$  and  $2\frac{1}{2}$  parts of  $\text{FeSO}_4$  is added to a neutral or slightly alkaline solution of an iodide, a white precipitate of cuprous iodide,  $\text{CuI}$ , is formed. The  $\text{FeSO}_4$  is added, to convert the  $\text{Cu}''\text{SO}_4$  into  $\text{Cu}'\text{SO}_4$ . The addition of a small quantity of a solution of  $\text{Na}_2\text{CO}_3$ , so as to render the solution slightly alkaline, promotes the complete precipitation of the I. Chlorides and bromides are not precipitated by this reagent.

488. A bead of  $\text{NaNH}_4\text{HPO}_4$  saturated with  $\text{CuO}$ , if mixed with a substance containing I, and ignited in the inner blowpipe flame, imparts an intense GREEN COLOR to the flame.

### IODIC ACID, $\text{HIO}_3$ .

489. This acid is a white crystalline solid; it is decomposed at a moderate heat into O and I; it is readily soluble in water. Its salts are decomposed by heat, a metallic iodide and free oxygen being formed, or into iodine, oxygen, and a metallic oxide; the alkaline iodates are the only salts of this acid which dissolve readily in water.  $\text{AgNO}_3$  and  $\text{BaCl}_2$  precipitate it from its solutions.

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\* A solution of  $\text{N}_2\text{O}_4$  in  $\text{H}_4\text{SO}_4$  may be employed in place of the  $\text{KNO}_2$  and  $\text{HCl}$ . Fresenius states that a single drop on a glass rod of the  $\text{N}_2\text{O}_4$  solution suffices to produce the reaction most distinctly.

490.  $\text{SO}_2$  and  $\text{H}_2\text{S}$  each throw down I from solutions of  $\text{HIO}_3$ ; if an excess of either reagent is added, the I becomes converted into HI.

491. An iodate can be detected in the presence of an iodide by the simple addition of a strong acid; the HI and  $\text{HIO}_3$  act upon each other in the following manner:  $5\text{HI} + \text{HIO}_3 = 3\text{I}_2 + 3\text{H}_2\text{O}$ .

### HYDROBROMIC ACID, HBr.

*Solution for the reactions, KBr in water.*

492. Br at the ordinary temperature is a liquid of a deep red color; it is soluble in water, but it is much more soluble in alcohol, ether, chloroform, and bisulphide of carbon; the solutions are reddish-yellow. Br, especially in its vaporous state, turns moistened starch yellow; the yellow color does not always appear instantaneously. HBr is a gas which closely resembles in its properties HCl gas. It emits in the air white fumes, which are denser than those produced by HCl; it is decomposed by Cl, Br being set free, and HCl formed; the liberated Br appears under the form of reddish vapors, or condenses into reddish drops. HBr is extremely soluble in  $\text{H}_2\text{O}$ ; the solution is colorless, unless it contains free Br, which it dissolves in large quantities; it has then a dark reddish color. HBr, in the gaseous state, may be obtained by heating KBr with  $\text{H}_3\text{PO}_4$ , or by acting on  $\text{PBr}_3$  with water, HBr and phosphorous acid,  $\text{H}_3\text{PO}_3$ , being formed. It may be obtained in solution by passing  $\text{H}_2\text{S}$  through water which contains Br. The bromides are solid at ordinary temperatures; most of them are fused by a moderate heat, and are partially volatilized; the bromides of Au and Pt are decomposed by heat; most of the bromides are readily soluble in water.

493. HBr and the bromides, with the exception of AgBr and HgBr, are decomposed by  $\text{HNO}_3$ , on the application of heat, the H or the metal being oxidized and the Br liberated; if the bromide operated upon is in the solid state or as a concentrated solution, the Br vaporizes; but if the bromide is in a state of solution and not very concentrated, the Br dissolves in the liquid, coloring it yellow or yellowish-red. In the cold,  $\text{HNO}_3$ , even the fuming red acid, does not liberate Br from moderately dilute solutions of the bromides, nor is it liberated by a solution of  $\text{N}_2\text{O}_4$  in HCl, or by  $\text{H}_2\text{SO}_4$  and  $\text{KNO}_3$ .

494. Cl, in the *gaseous state* or in *solution*, immediately liberates Br in the solutions of its compounds; the fluid assuming a yellowish-red tint if the quantity of Br present

is not too minute. A large excess of Cl must be avoided, since this will cause the formation of chloride of bromine, which will destroy the color wholly or nearly so. This reaction is made much more delicate by addition of a fluid which dissolves Br and does not mix with water, as sulphide of carbon or chloroform. Mix the neutral or feebly acid solution in a test-tube with a little of one of these fluids, sufficient to form a large drop at the bottom, then add dilute chlorine water drop by drop, and shake the tube. With appreciable quantities of Br, for example 1 part in 1000 parts of water, the drop at the bottom acquires a reddish-yellow tint. A large excess of chlorine-water must be avoided, and it must always be first ascertained whether, when mixed with a large quantity of water and some sulphide of carbon or chloroform, and shaken, it leaves these reagents quite uncolored; if it does not, it ought not to be employed. If the solution of Br in sulphide of carbon or chloroform is mixed with a solution of KHO, the mixture shaken, and heat applied, the yellow color will disappear, KBr and potassic bromate,  $\text{KBrO}_3$ , being formed. By evaporating this solution to dryness and igniting the residue, the  $\text{KBrO}_3$  will be converted into KBr. On heating the bromide with  $\text{MnO}_2$  and  $\text{H}_2\text{SO}_4$  in a small retort, YELLOWISH-RED VAPORS will be evolved unless the quantity be very minute. These vapors, when brought in contact with *starch paste*, will communicate to it an ORANGE-YELLOW COLOR, which disappears on exposure to the air.\*

495. Br in presence of I and Cl may be identified by the following simple operation: Mix the fluid with a few drops of dilute  $\text{H}_2\text{SO}_4$ , then with some starch paste, and add a little red fuming  $\text{HNO}_3$ , or, better still, a solution of  $\text{N}_2\text{O}_4$  in  $\text{H}_2\text{SO}_4$ , whereupon the iodine reaction will show itself immediately. Add now chlorine-water drop by drop until that reaction has disappeared, then add some more chlorine-water to set the Br also free, which may then be separated and identified by means of chloroform or bisulphide of carbon, or the liberated I may also be taken up with chloroform or bisulphide of carbon, and chlorine-water cautiously added, when the violet-red coloration imparted by

\* Fresenius recommends that the fluid containing the free Br, or the mixture of bromide,  $\text{MnO}_2$ , and  $\text{H}_2\text{SO}_4$ , be gently heated in a very small beaker, covered with a watch-glass with a slip of paper attached to the lower side, moistened with starch paste, and strewed over with starch powder; in the course of a short time, if bromine is present, a yellow tint will be imparted to the starch.

the iodine gradually fades away, and after its disappearance the brownish-yellow color given by the Br is distinctly visible.—*Fresenius*.

496. Solid bromides, when distilled with  $K_2Cr_2O_7$  and concentrated  $H_2SO_4$ , yield pure Br, which becomes colorless, or nearly so, when treated with excess of  $NH_4HO$ ; by this means it is distinguished from chlorochromic acid, which it resembles in color. (See par. 474.)

497. If a  $NaNH_4HPO_4$  bead saturated with  $CuO$  is mixed with a substance containing Br, and then ignited in the inner blowpipe flame, the flame is colored BLUE, inclining to GREEN, more particularly at the edges.—*Berzelius*.

### HYDROCYANIC ACID (*Prussic Acid*), $HCN$ or $HCy$ .

*Solution for the reactions,  $KCy$  in water.*

498. In its anhydrous state  $HCy$  is a colorless, volatile, inflammable liquid, possessing a strong odor resembling oil of bitter almonds; it boils about  $27^\circ C.$ , and evaporates in large quantities far below its boiling-point; a small quantity of the vapor is sufficient to produce instantaneous death. Water dissolves it in all proportions; the solution is liable to undergo decomposition if exposed to the light, the decomposition taking place more quickly as the acid is stronger; alkalis accelerate the decomposition, but the presence of a small quantity of  $HCl$  impedes decomposition; concentrated  $HCl$ , on the other hand, decomposes  $HCy$  immediately into  $NH_4Cl$  and  $HCHO_2$  (formic acid); concentrated  $H_2SO_4$  produces the same decomposition, but further converts the  $HCHO_2$  into  $CO$  and  $H_2O$ . Although  $HCHO_2$  is one of the products of decomposition of  $HCy$ ,  $NH_4CHO_2$  (ammonic formate) is converted by heat into  $HCy$  and  $H_2O$ ; on boiling  $HCy$  with an excess of  $KHO$ ,  $NH_3$  is evolved and  $KCHO_2$  remains in solution. "To prepare a solution of  $HCy$  the usual plan is to decompose in solution  $K_4FeCy_6$  by dilute  $H_2SO_4$ , and distil; the best proportions are 10 parts of crystallized  $K_4FeCy_6$  dissolved in 50 parts of  $H_2O$ ; 3.5 parts of common  $H_2SO_4$  are then mixed with 25 parts of  $H_2O$ , and the mixture, when cold, is poured into the solution of the salt, and then distilled; the equation explains the reaction:  $2K_4FeCy_6 + 3H_2SO_4 + Aq = 6HCy + K_2Fe_2Cy_6 + 3K_2SO_4 + Aq$ ." The solution of  $HCy$  is feebly acid to test-paper; it does not decompose the alkaline carbonates; it readily dissolves  $HgO$ , forming  $HgCy_2$ , and, when mixed with a solution of the

alkalies, alkaline cyanides are formed, which are soluble in water; their solutions are alkaline to test-paper, and they are decomposed with the liberation of  $\text{HCy}$  by the weakest acid.  $\text{HgCy}_2$  is soluble in water; most of the cyanides of the other heavy metals are insoluble. Some of the cyanides give off  $\text{HCy}$  when treated with dilute solutions of the stronger mineral acids; others, as ferrous and aurous cyanides, may be boiled with moderately strong acids without decomposition. Most of the insoluble cyanides dissolve in solutions of the alkaline cyanides, forming double cyanides.  $\text{KCy}$  and  $\text{NaCy}$  sustain a red heat without decomposition, if air and moisture be excluded; heated in contact with the air, they are converted into cyanates,  $\text{M}'\text{CyO}$ , and when further heated into carbonates.  $\text{AgCy}$  and  $\text{HgCy}_2$ , on being heated give off  $\text{Cy}$  as gas; other cyanides give off  $\text{N}$ , a mixture or compound of  $\text{C}$  and the metal being left. All the cyanides, when heated in the presence of water, are destroyed; the alkaline cyanides are converted by continued boiling with water into  $\text{NH}_3$  and alkaline formates.

499. If to a solution of  $\text{HCy}$  or an alkaline cyanide  $\text{KHO}$  and a mixed solution of a ferrous and ferric salt be added, a greenish-blue precipitate will be produced; on the addition of  $\text{HCl}$  *insoluble Prussian blue* separates. If only a very minute quantity of  $\text{HCy}$  is present, the fluid simply appears green after the addition of the  $\text{HCl}$ , and it is only after long standing that a trifling blue precipitate separates from it.\*

500. "If to a solution of  $\text{HCy}$   $\text{KHO}$  is added in excess, and then finely pulverized  $\text{HgO}$ , the latter dissolves as readily as it would in free  $\text{HCy}$ . Since  $\text{HgO}$  is soluble in solutions of the alkalies *only in presence of*  $\text{HCy}$ , this reaction may be looked upon as a positive test for that acid."—*Fresenius*.

501. When  $\text{HCy}$  is added to  $(\text{NH}_4)_2\text{S}$  containing an excess of  $\text{S}$ , ammonie sulphocyanide,  $\text{NH}_4\text{CyS}_2$ , is formed, which gives a *deep blood-red color* with ferric salts (179). This test may be applied in qualitative analysis in the following way: Add a few drops of *yellow*  $(\text{NH}_4)_2\text{S}$  to the

\* This test may be modified by heating gently the suspected mixture with  $\text{H}_2\text{SO}_4$ , and suspending in the flask or retort, for a few minutes, a piece of paper moistened with a solution of  $\text{KHO}$ ; on dropping a weak solution of the mixed iron salts upon the paper, and immersing it in diluted  $\text{H}_2\text{SO}_4$ ,  $\text{HCy}$  may be recognized by the formation of Prussian blue when very minute traces only are present.—*Miller*.

liquid supposed to contain the  $\text{HCy}$ ; evaporate at a *gentle heat* (not above  $100^{\circ}\text{C.}$ ), until the excess of  $(\text{NH}_4)_2\text{S}$  has completely volatilized, which is ascertained by the smell; then test the solution with a drop or two of  $\text{Fe}_2\text{Cl}_6$ . This test is exceedingly delicate. "If an acetate is present, the reaction takes place only upon addition of  $\text{HCl}$ ."—*Fresenius*.

502. By neither of the above methods will  $\text{Cy}$  be discovered in  $\text{HgCy}_2$ ; the solution of  $\text{HgCy}_2$  must be treated with  $\text{H}_2\text{S}$ ,  $\text{HgS}$  will be precipitated, and  $\text{HCy}$  remain in solution; examine then for  $\text{HCy}$  according to pars. 499, or 501, or 503.

503. Schönbein has recently proposed a new and exceedingly delicate test for this acid; it consists of paper imbued with resin of guaiacum, and moistened with a solution of  $\text{CuSO}_4$ , in contact with this acid the prepared paper immediately assumes a *blue color*. To employ this test a slip of the paper imbued with guaiacum is moistened with the solution of  $\text{CuSO}_4$ , and brought in contact with  $\text{HCy}$ , either dissolved in water or diffused in the air, when it immediately becomes blue; the color developed on the paper remains for a long time, but diminishes as the paper dries. After several days it passes to a greenish-gray, but revives slightly on moistening the paper.

504. *Detection of the acid in organic mixtures*.—Place the suspected mixture in a wide-mouthed bottle. (1) Introduce into the atmosphere of the bottle Schönbein's paper. (2) Smear a glass plate with a drop of yellow ammoniac sulphide, and place it over the mouth of the bottle; subsequently evaporate the excess of  $(\text{NH}_4)_2\text{S}$  at a low temperature, and proceed as directed at par. 501. (3) Smear a glass plate with a mixture of  $\text{KHO}$  and  $\text{FeSO}_4$ , and place it over the mouth of the bottle for a few minutes, then acidify with  $\text{HCl}$  (par. 499). "In order to obtain the acid from the coats of the stomach or its contents, the substance, cut into small pieces, should be mixed with cold distilled water, and distilled by a water-bath at a low temperature ( $77^{\circ}\text{C.}$ ), the distillate being collected in a *cold* receiver; if the suspected liquid is alkaline, a small quantity of tartaric acid may be added to neutralize it; the distillate may then be examined by the three preceding tests."

NITRIC ACID,  $\text{HNO}_3$ .

*Solution for reactions,  $\text{KNO}_3$ , in water.*

505.  $\text{HNO}_3$ , when pure, is a colorless liquid, boiling at  $86^\circ \text{C}$ . with partial decomposition, a weaker acid being left behind; it fumes strongly in the air, and absorbs water from it, but with less avidity than  $\text{H}_2\text{SO}_4$ . It is frequently of a yellowish or red color, owing to the presence of some of the lower oxides of nitrogen. Owing to the facility with which it gives up oxygen, it is, especially when heated, a most powerful oxidizing agent; its action upon the metals has been already noticed, it acts more or less powerfully on all the solid non-metallic elements. It acts with great energy on most organic bodies, the kind of action varying with the strength of the acid and the temperature; organic substances containing nitrogen are stained yellow by the acid. NITRIC ANHYDRIDE ( $\text{N}_2\text{O}_5$ ) is a very unstable body.

506. All the neutral nitrates are soluble in water; a few of the basic salts are insoluble in that liquid, the solutions of the nitrates of the metals of the alkalies and alkaline earths, and of silver and manganese are neutral to test-paper. Most of the nitrates fuse readily when heated; they are all decomposed at an elevated temperature; "the nitrates of the highly basylous metals at first give off nearly pure  $\text{O}$ , and are converted into nitrites, afterwards a mixture of  $\text{O}$  and  $\text{N}$ , together with some nitric peroxide ( $\text{N}_2\text{O}_4$ ). Other nitrates, which decompose at a lower temperature, those of  $\text{Hg}$ ,  $\text{Pb}$ , and  $\text{Ag}$ , for instance, evolve a mixture of  $\text{N}_2\text{O}_4$  and  $\text{O}$ . A few still more easily decomposable hydrated salts, aluminic and bismuthic trinitrates, for instance, give off  $\text{HNO}_3$ . Ignited  $\text{AgNO}_3$  leaves a residue of  $\text{Ag}$ , but most normal nitrates, when strongly heated, leave residues of oxides analogous in composition to the original salt, but ferrous and manganous nitrates leave oxides richer in oxygen than those which correspond to the original salts, viz.  $\text{Fe}_2\text{O}_3$  and  $\text{Mn}_3\text{O}_4$ . Nitrates heated with combustible bodies produce a more or less violent deflagration or explosion. The acid-forming bodies, metallic or non-metallic, when deflagrated with nitre, leave potassic or sodic salts of the respective acids."

507. To detect  $\text{HNO}_3$  in a solution, add to it one-fourth of its volume of undiluted  $\text{H}_2\text{SO}_4$ , and *gently warm* the solution; a solution of a ferrous salt must then be added,

along with a few drops more of the  $\text{H}_2\text{SO}_4$ , when the liquid will become of a deep brown color, attended, most likely, with an energetic disengagement of gas; the color, in this case, will soon disappear, for a reason presently to be named, but can readily be reinstated by a fresh addition of the ferrous solution. Or the solution of the ferrous salt may be added first to the solution of the nitrate, and then the undiluted  $\text{H}_2\text{SO}_4$  poured in, in such a way that it forms a layer at the bottom of the test-tube; in this case the deep-brown color will be produced at the contact-surface of the two liquids. The dark brown color is owing to the formation of a compound of nitric oxide ( $\text{NO}$ ) and the ferrous salt, the formula of the compound being  $2\text{Fe}''\text{SO}_4\text{NO}$ ; this compound is destroyed by heat with the disengagement of the  $\text{NO}$ , hence the fading of the color when the solution is heated.

508. When nitrates are heated with undiluted  $\text{H}_2\text{SO}_4$ , in the presence of *copper turnings*,  $\text{NO}$  is evolved, which, in contact with the air, forms red fumes, owing to its absorption of oxygen and its conversion into nitrous anhydride ( $\text{N}_2\text{O}_3$ ) and nitric peroxide ( $\text{N}_2\text{O}_4$ ). This experiment ought to be conducted in a narrow test-tube. The color is best observed by looking into the test-tube lengthways.

509. The following is an exceedingly delicate test for detecting  $\text{HNO}_3$ , it is therefore specially adapted for detecting the acid in water. Dissolve brucin in 1000 times its weight of water, pour about 15 grains of this solution into a test-tube, then add a little of the water to be tested, and lastly, some  $\text{H}_2\text{SO}_4$ ; the acid is made to flow down the side of the tube so as to gather beneath the water. At the place of contact of the two liquids a rose-red zone immediately forms; if  $\text{HNO}_3$  be present in detectable quantity. The reagents must be specially purified before they can be employed. The water employed to dissolve and wash the brucin must be repeatedly rectified over  $\text{KHO}$ . The brucin is washed with the pure water several times to remove nitrates. The  $\text{H}_2\text{SO}_4$  is mixed with 5 per cent. of  $\text{NH}_4\text{HCO}_3$ , and three-fourths distilled off in a glass vessel. —*Kersten*.

510. The following has recently been proposed as a delicate test for nitrates, and, therefore, specially applicable for their detection in water. Into a test-glass about 1 cub. cent. of pure concentrated  $\text{H}_2\text{SO}_4$  is placed (sp. gr. 1.84), to this is added drop by drop  $\frac{1}{2}$  cub. cent. of a solution of sulphate of aniline prepared by adding 10 drops of aniline



of commerce to 50 cub. cent. of dilute  $\text{H}_2\text{SO}_4$  diluted in the proportion of 1 of acid to 6 of water. A glass rod is dipped into the liquid to be tested and then into the test-glass; on moving the stirrer about gently, when the slightest trace of  $\text{HNO}_3$  is present, red streaks mark the course of the glass rod; when there is slightly more than the merest trace, the liquid becomes carmine tinted; and with a still further quantity a deep red tint, which turns reddish-brown. Hyponitric acid produces the same reaction.

511. Dissolve 1 part of carbolic acid (phenol) in 4 parts of concentrated  $\text{H}_2\text{SO}_4$ , and dilute the solution with 2 parts of water. If the substance to be examined for  $\text{HNO}_3$  is in solution, evaporate it in a porcelain crucible or its cover, and let fall one or two drops of the phenyl-sulphuric acid solution upon the residue at a temperature of about  $100^\circ \text{C}$ . By the excess of the  $\text{H}_2\text{SO}_4$  any nitrates, if present, will be decomposed, and the  $\text{HNO}_3$  derived from them will directly form nitro-compounds with the phenol, which are indicated by the production of a reddish-brown color. When neither organic matters, nor compounds of Cl, I, and Br, from which  $\text{H}_2\text{SO}_4$  easily separates carbon or the haloids, are present, this coloration is in itself conviucing. But for fear of their presence, it is better, in all cases, to add a drop or two of strong  $\text{NH}_4\text{HO}$  to the colored product, when the haloids will be dissolved in the form of colorless salts, and the carbon remain suspended in the small particles, not interfering with the recognition of the characteristic yellow solution of the nitro-phenylate of ammonia. Frequently, after the addition of  $\text{NH}_4\text{HO}$ , there appears instead of a yellow an unstable emerald-green color, which changes into a rose color after the addition of an acid and occasionally becomes greenish-yellow.—*Sprengel*.

512. When a minute quantity of *gold-leaf* is boiled in  $\text{HCl}$ , no action is produced; but on the addition of a little  $\text{HNO}_3$ , or a nitrate, the gold quickly disappears and may be detected in solution by the method described in par. 284.

513. When a moderately concentrated solution of  $\text{KHO}$  is poured upon a mixture of Zn and Fe, H is freely disengaged, even without the application of heat; if a nitrate is added to this mixture evolving the H, it is followed by an immediate development of ammonia. This reaction furnishes a good qualitative test of the presence of nitric or nitrous acid. The fluid to be examined is reduced to a small bulk, and poured into a test-tube containing two or three grammes of a mixture of granulated zinc and clean

iron filings. A small quantity of strong KHO solution is added, and the whole heated to boiling. The usual tests for ammonia may be applied at the mouth of the tube.—*Harcourt*.

514. Very minute quantities of  $\text{HNO}_3$  may be detected by reducing it first to nitrous acid which may be effected both in the moist and the dry way; in the former by treating the solution of the  $\text{HNO}_3$  or of the nitrate for some time with finely divided zinc, best with zinc amalgam, and then filtering (*Schönbein*); in the dry way by fusing the substance under examination with  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  at a moderate heat, exhausting the mass, after cooling, with water, and filtering. Upon adding either of the filtrates to a solution of KI, mixed with starch and dilute  $\text{H}_2\text{SO}_4$ , the fluid acquires a blue color from iodide of starch; see pars. 485 and 486.—*Fresenius*.

515. If a mixture of nitrate with KCN in powder is heated upon platinum foil, a violent deflagration will ensue, owing to the sudden evolution of  $\text{CO}_2$  and N, produced by the oxidation of the CN. Very minute quantities of nitrates may be detected in this way.

### NITROUS ACID, $\text{HNO}_2$ .

516. Nitrites give a *brown color* with ferrous salts without the addition of an acid. Acidulated solutions of nitrites produce at once a purple color with starch and KI. The *nitrates* do not color ferrous salts brown or decompose KI until the nitric acid has been liberated and reduced to nitrous acid by warming with sulphuric acid.

517. Nitrites are, like nitrates, oxidizing agents, but they act more readily than the latter. Nitrites act also as reducing agents, acidulated solutions decolorize potassic permanganate, and gradually change potassic bichromate to a greenish hue: they also reduce  $\text{AuCl}_3$  and mercurous salts; these reducing actions distinguish them from nitrates.

### CHLORIC ACID, $\text{HClO}_3$ .

518. This acid, in its concentrated state, appears in the form of a yellow syrupy liquid, the odor of which resembles that of  $\text{HNO}_3$ ; the dilute acid is colorless and inodorous.  $\text{HClO}_3$  is an unstable acid, it gradually undergoes decomposition on exposure to light; at a temperature of  $40^\circ \text{C}$ . it undergoes decomposition, and at  $100^\circ \text{C}$ ., or a little above, it is rapidly converted into perchloric acid ( $\text{HClO}_4$ ), oxygen, chlorine, and water:  $3\text{HClO}_3 = \text{HClO}_4 + \text{Cl}_2 + 2\text{O}_2 + \text{H}_2\text{O}$ .

It is decomposed by contact with organic matter; it is

a very powerful oxidizing and bleaching agent; it reddens litmus first and afterwards bleaches it. CHLORIC ANHYDRIDE has not been obtained.

519. All the chlorates are soluble in water; they are decomposed upon ignition, oxygen being given off, and generally the metal is left as a chloride; but in the case of magnesia and some other chlorates the metal is left as an oxide, Cl and O being given off:  $2\text{MgClO}_3 = 2\text{MgO} + \text{Cl}_2 + 2\text{O}_2$ .

Fused chlorates are powerful oxidizing agents; when heated with organic substances, they deflagrate with far greater violence than the nitrates. The solutions of the chlorates of the metals of the alkalies and alkaline earths are neutral to test-paper.

520. To detect this acid, add to a small quantity of the solid substance under examination a few drops of *undiluted*  $\text{H}_2\text{SO}_4$  in the cold. The chlorate will be decomposed,  $\text{KHSO}_4$  and POTASSIC PERCHLORATE ( $\text{KClO}_4$ ) being formed, along with a GREENISH-YELLOW COLORED explosive gas, perchloric oxide ( $\text{Cl}_2\text{O}_7$ ), which escapes:  $3\text{KClO}_3 + 2\text{H}_2\text{SO}_4 = \text{KClO}_4 + \text{Cl}_2\text{O}_7 + 2\text{KHSO}_4 + \text{H}_2\text{O}$ , the application of heat must be avoided, and the quantities operated upon should be small, to prevent any loud and violent explosion taking place.

521. If the solution of a chlorate is colored light blue, with some solution of indigo in sulphuric acid, a little dilute  $\text{H}_2\text{SO}_4$  added, and a solution of sulphite of soda dropped cautiously into the blue fluid, the color of the indigo disappears immediately. The cause of this equally characteristic and delicate reaction is, that the sulphurous acid deprives the chloric acid of its oxygen, and the liberated chlorine decolorizes the indigo. (*Fresenius*.) This test readily distinguishes chlorates from nitrates.

522. Upon heating chlorates with  $\text{HCl}$  the constituents of the two acids decompose, forming water, chlorine, and an oxide of chlorine. The test-tube in which the experiment is made becomes filled in this process with a greenish-yellow gas, of a very disagreeable odor, resembling that of chlorine; the  $\text{HCl}$  acquires a greenish-yellow color.

523. If a mixture of chlorate and  $\text{KCy}$  is gently heated upon platinum foil, a very violent deflagration ensues, even with a minute quantity of chlorate. The experiment must only be made with very minute quantities of chlorate.

CLASSIFICATION OF THE INORGANIC ACIDS, INCLUDING  
OXALIC ACID, WITH A DESCRIPTION OF THE PROCESSES  
TO BE FOLLOWED IN THE EXAMINATION OF SUBSTANCES  
FOR THESE ACIDS.

524. *Classification of the acids.*—The inorganic acids described in this book may be conveniently divided into four groups, as follows:—

FIRST GROUP.

1st Division.—Acids which are precipitated by  $\text{H}_2\text{S}$  from acid solutions, as *Sulphides*—ARSENIOUS and ARSENIC ACIDS.  
2d Division.—Acid which is converted by  $\text{H}_2\text{S}$  into a base—CHROMIC ACID. The acids contained in this group are detected in testing for the bases. ARSENIOUS and ARSENIC ACIDS, being precipitated by  $\text{H}_2\text{S}$ , are classed amongst the bases; whilst CHROMIC ACID is converted into  $\text{Cr}_2\text{O}_3$ , a member of the fourth group of bases; the change of color attending this conversion is so characteristic, that it cannot be overlooked by the most inexperienced student. The only thing which can cause the least difficulty or perplexity is the mistaking a green solution, with a light-colored precipitate suspended in it, for a green precipitate.

SECOND GROUP.

525. 1st Division.—Acids which are precipitated by  $\text{BaCl}_2$ , or any soluble baric salt from *neutral*, but not from *acid*, solutions, their baric salts being soluble in acids. The members of the 1st group, and likewise PHOSPHORIC, OXALIC, HYDROFLUORIC, BORACIC, SILICIC, and CARBONIC ACIDS.\*  
2d Division.—Acid which is precipitated by  $\text{BaCl}_2$ , or any soluble baric salt from *acid*, as well as *neutral* solutions—SULPHURIC ACID.

(a) All these baric salts are *colorless*, with the exception of BARIC CHROMATE, which is of a *pale-yellow color*. If arsenious, arsenic, or chromic acid has been detected in

\* Baric borate, also baric oxalate and fluoride, are soluble in solutions containing ammonio salts; the last two are soluble in a less degree than the baric borate. A borate, oxalate or fluoride may be present in a solution which gives no precipitate on the addition of a soluble baric salt, if ammonio salts are present.

examining for the bases, it should be got rid of from the portion of the solution to which the baric and silver salts are to be added by *slightly* acidifying the solution with  $\text{HNO}_3$ , if it is not acid to test-paper, and treating it with an excess of  $\text{H}_2\text{S}$ , filtering if necessary, gently boiling the solution until the excess of  $\text{H}_2\text{S}$  is removed, and neutralizing it with  $\text{NH}_4\text{HO}$ . If  $\text{CO}_2$  has been detected in testing for the bases, it is better to get rid of it also before adding the baric salt, by adding, as before,  $\text{HNO}_3$  until it is slightly in excess, and then boiling for a short time; and, as before, neutralizing the solution with  $\text{NH}_4\text{HO}$ . To the *neutral* solution thus prepared, if one or all of these four acids were present, or to the *neutral* solution if they are not present, a solution of  $\text{BaCl}_2$  is added, or if an argentic or mercurous compound is present, a solution of  $\text{Ba}(\text{NO}_3)_2$ ; if no precipitate is formed the acids of this group, with the exception of those got rid of, are absent;\* if a precipitate is produced add *dilute*  $\text{HCl}$ , or *dilute*  $\text{HNO}_3$ , if  $\text{Ba}(\text{NO}_3)_2$ † has been employed; if the whole of the precipitate, or a portion of it, is dissolved, one or more of the acids whose baric salts are soluble in acids are present; if the whole or a portion of it is insoluble in acids,  $\text{H}_2\text{SO}_4$  or a *sulphate is present*.

### THIRD GROUP.

526. 1st Division.—Acids which are precipitated from *neutral*, but not from *acid*, solutions by  $\text{AgNO}_3$ . The members of the 1st and 2d groups, with the exception of **SULPHURIC ACID**. 2d Division.—Acids which are precipitated from *acid* as well as *neutral* solutions—**HYDROSULPHURIC, HYDROCHLORIC, HYDROBROMIC, and HYDRIODIC ACIDS**.

The following silver salts are colored: **ARGENTIC SULPHIDE**, *black*; the **CHROMATE**, *red*; the **ARSENATE**, *reddish-brown*; the **ARSENITE**, **PHOSPHATE**, and **IODIDE**, *yellow*; the **SILICATE**, *yellow or white*; the **BROMIDE**, *yellowish-white*. The silver salts of the rest of the acids of the group are colorless. Besides removing the acids of the 1st group

\* The absence of the acids whose baric salts are soluble in ammoniac salts, if these are present, is not established by this experiment (see note, page 208).

† Concentrated  $\text{HCl}$  or  $\text{HNO}_3$  must not be employed, because  $\text{BaCl}_2$  and  $\text{Ba}(\text{NO}_3)_2$  are insoluble in them, and would therefore separate from the solution.

and  $\text{CO}_2$ , it is necessary also to get rid of a sulphide before adding the *silver salt*, and as *ferrous sulphate* reduces the silver salt, Ag being precipitated, it is necessary to convert it, if it is present, into the *ferric state*; the solution must, therefore, be rendered slightly acid, if it is not so already, with  $\text{HNO}_3$ ; it must then be treated with an excess of  $\text{H}_2\text{S}$ , if any of the members of the 1st group of acids are present, and filtered if necessary; the solution must be gently boiled to expel the  $\text{H}_2\text{S}$  and  $\text{CO}_2$ , and to convert the ferrous salt into the ferric state;  $\text{NH}_4\text{HO}$  must then be added to the solution slightly in excess, and the solution again boiled until it is *neutral* to test-paper; if a precipitate has been formed, filter and add a solution of  $\text{AgNO}_3$  to the clear liquid. If the solution becomes acid after the addition of the silver solution, it ought to be *very carefully* neutralized with  $\text{NH}_4\text{HO}$ ; if no precipitate is produced by  $\text{AgNO}_3$ , *all the acids* of the group, with the exception of those got rid of, are *absent*. If a precipitate is produced, its color ought to be observed;  $\text{HNO}_3$ , entirely free from  $\text{HCl}$ , must be added, and the mixture shaken; if the whole of the precipitate or a portion of it is dissolved, one or more of the acids whose silver salts are soluble in  $\text{HNO}_3$  are present; if the whole or a portion of the silver precipitate is insoluble in  $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ ,  $\text{HCN}$ , or their radicals, may be present. As  $\text{AgNO}_3$  causes no precipitate in solutions of mercuric cyanide, if  $\text{Hg}$  in the mercuric state is present, cyanogen may be present, although  $\text{AgNO}_3$  produces no precipitate; cyanogen must, therefore, be examined for according to par. 502, when mercury is present.

When the silver precipitate does not entirely redissolve in  $\text{HNO}_3$ , examine the original solution for  $\text{Cy}$ ,  $\text{I}$ ,  $\text{Br}$ , and  $\text{Cl}$ .

#### FOURTH GROUP.

527. Acids which are not precipitated by any reagent—**NITRIC and CHLORIC ACIDS.** A special examination must always be made for the acids contained in this group.

528. We will now give directions for testing for each acid individually by means of characteristic tests, and afterwards the methods to be pursued in preparing solutions for the examination of the acids.

## CHARACTERISTIC TESTS FOR THE INORGANIC ACIDS.

529. The characteristic tests must be applied to the original solution; a separate portion must be taken for each acid.

530. ARSENIOS ACID, ARSENIC ACID, CHROMIC ACID.—As these acids are discovered in testing for the bases, no experiments require to be made for their detection when testing for the acids.

531. SULPHURIC ACID.—The presence or absence of this acid is ascertained on testing a part of the solution with the general reagent,  $\text{BaCl}_2$ , and if a precipitate is produced digesting it in dilute  $\text{HCl}$  or  $\text{HNO}_3$ , if it dissolves the acid is absent, if it does not dissolve it is present (404).

532. BORACIC ACID.—This acid can be detected in most cases, by the method described in par. 419; but the most certain test is the one described in par. 420.

533. PHOSPHORIC ACID.—When the phosphates are soluble in ammoniac solutions (and the student can decide this when he knows what bases are present), this acid can be detected by the method described in par. 424, but the most certain tests are 427 and 428, especially the last. The student must, however, remember that arsenic acid gives precipitates with these reagents, similar to those given by phosphoric acid; when present, it must, on this account, be removed from the solution by  $\text{H}_2\text{S}$ , or be reduced to the state of arsenious acid, before testing for phosphoric acid.  $\text{PO}_4$  may also be detected by the method given in par. 431.

534. CARBONIC ACID.—This acid is distinguished from the other gaseous acids by giving a precipitate with lime-water; the way for evolving the gas, when combined, and testing it when liberated, with lime-water, is described in pars. 441 and 442.

535. OXALIC ACID.—This acid is detected by the method described at 449; but very minute quantities of it are more securely detected by boiling the substance with a solution of  $\text{Na}_2\text{CO}_3$ , for some time; subsequently filtering, and acidifying the filtrate with acetic acid, and then adding to it a solution of  $\text{CaSO}_4$  (451).

536. SILICIC ACID.—To test for this acid, evaporate the solution to dryness with an acid, and proceed as directed at 453 or 455.

537. HYDROFLUORIC ACID.—Test for this acid, when silicic acid is absent, by the method described at 460;

when silicic acid is present, by the one described at 462 or 463.

538. **SULPHIDE OF HYDROGEN.**—This acid is distinguished from the other gaseous acids by giving, with soluble salts of silver and lead, black precipitates; the way for applying the test is described in par. 468. The sulphur in sulphides which are not decomposed by  $\text{HCl}$ , but require for their decomposition  $\text{HNO}_3$ , or aqua regia, cannot be detected in this way: recourse must be had in these cases to the process described in par. 471.

539. **HYDROCHLORIC ACID.**—When  $\text{HBr}$  and  $\text{HCy}$  are absent the presence of this acid is proved by the insolubility of the silver precipitate in  $\text{HNO}_3$ , and by its solubility in  $\text{NH}_4\text{HO}$ ; when  $\text{HCy}$  is present, and  $\text{HBr}$  absent, its presence is proved, if, after igniting the silver precipitate, which was insoluble in  $\text{HNO}_3$  but soluble in  $\text{NH}_4\text{HO}$ , a whitish residue remains, which is insoluble in  $\text{HNO}_3$ . When  $\text{HBr}$  is present, no matter whether  $\text{HCy}$  is present or absent, the presence of  $\text{HCl}$  can only be ascertained by the test described at 474.

540. **HYDRIODIC ACID.**—Iodine is best discovered by the test described at 486.

541. **HYDROBROMIC ACID.**—Examine for  $\text{Br}$ , according to the method given in par. 494; in the presence of  $\text{I}$  or  $\text{Cl}$ , according to par. 495.

542. **HYDROCYANIC ACID.**—This acid can be distinguished from all other acids by the tests described in pars. 499, 501, and 503; if, however mercuric compounds are present which will have been discovered in testing for the bases, the process described in par. 502 must be employed.

543. **NITRIC ACID.**—The tests described at 507, 508, 512, 513, or 514, may be employed, but for the detection of the acid in waters the tests described at pars. 509 and 510 are the best.

544. **CHLORIC ACID.**—The presence or absence of this acid is proved by the tests described at 521 and 522.

545. *Preparation of the solutions and examination for the acids.*

The examination for the metallic or basic constituents must always precede the examination for the acids, for in the search for acids, the student will be greatly assisted by knowing what basic substances are present, which of their salts are soluble in water, and the reaction of the aqueous solutions of those salts on vegetable colors, also which of the salts of the metals found are insoluble in



water, but soluble in acids, and which of them are insoluble both in water and acids. He will, from a knowledge of the metals present, the solubility or insolubility of the substance under examination in water or acids, be able to form a tolerably correct conclusion as to the acid or acids which must be absent; thus, for instance, if the substance is a solid soluble in water, or it is a solution, water being the solvent, and the solution in either case is *neutral* to test-paper and the basic constituents present are K, Na and  $\text{NH}_4$ , all the acid radicals whose salts of K, Na and  $\text{NH}_4$ , are alkaline to test-paper must be absent, and if any polybasic acid radical is present which class of salts of this radical it is that is present will also be known. To take another example: if Ba, K, and Na were the metals present, and the solution was neutral to test-paper, all the acid radicals whose baric salts are *insoluble* in water, and all the soluble salts of Ba, K, and Na that are *alkaline* or *acid* to test-paper, must be absent. Again,  $\text{SO}_4$  or Cl need not be sought for in soluble compounds containing Ba or Ag respectively.

546 If the substance is a solid soluble in water, or it is a solution, water being the solvent, and if any of the members of the 1st group of acids or  $\text{CO}_2$ , or  $\text{H}_2\text{S}$ , have been detected, they must be got rid of and the solution neutralized as described at par. 525-a, the solution must then be examined for the other acids, as there directed. If none of the acids of the 1st group, nor  $\text{CO}_2$ , or  $\text{H}_2\text{S}$ , have been detected, proceed at once with the examination for the other acids according to par. 525-a, if the solution is *neutral*; if it is *alkaline*, first render it exactly neutral with  $\text{HNO}_3$ , and then proceed with the examination; if it is *acid*, neutralize it with  $\text{NH}_4\text{HO}$ ; filter, if necessary, and then proceed with the examination according to 525-a.

547. If the substance is insoluble in water but soluble in acids, or if it is a solution, an acid being the solvent, it is better in the majority of cases to get rid of all the metals but the alkaline ones, as the presence of some of the other metals interferes with the detection of some of the acids; they may be got rid of by one or other of the three following methods: 1. Precipitate the members of the 5th and 6th groups of bases, when they are present, from the acid solution with  $\text{H}_2\text{S}$ ; filter, boil the filtrate gently until the excess of  $\text{H}_2\text{S}$  is expelled, then add a solution of  $\text{Na}_2\text{CO}_3$  (entirely free from sulphate and chloride) in excess, and then a little  $\text{Na}_2\text{CO}_3$  in the solid state, and boil for some

time; 2d. Boil the *dry solid* with an excess of a concentrated solution of  $\text{Na}_2\text{CO}_3$ , for some time; 3d. Mix the solid with four parts of  $\text{NaKCO}_3$ , and fuse the mixture; boil the fused mass in water; whichever of these plans has been adopted the bases remain in the residue, and the acid radicals in combination with the Na; filter and add to the filtrate  $\text{HNO}_3$ , slightly in excess, heat the solution gently, taking care that it remains permanently acid, until all the  $\text{CO}_2$  is expelled, then add  $\text{NH}_4\text{HO}$ , slightly in excess, again warm the solution until it is *neutral* to test-paper; if a precipitate has been formed, filter and examine the clear solution according to par. 550.

548. It is not necessary to remove the bases in order to test for  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ , and  $\text{HNO}_3$ . All the chlorates are soluble in water, and so are all the nitrates, with the exception of a few basic ones; if a substance is, therefore, entirely insoluble in water, chlorates must be, and nitrates probably are, *absent*; if a portion only of a substance is soluble in water, treat a portion of the substance with water, and examine the aqueous solution *specially* for the acids of the 4th group.

549. In testing for the acids the general reagents are used in most cases only to prove the presence or absence of an entire group of acids. The detection of each of the acids in the groups requires the further application of the characteristic tests, par. 529.

550. Test a portion of the solution with one of  $\text{BaCl}_2$ , or  $\text{Ba}(\text{NO}_3)_2$ , as directed at par. 525; test another portion with one of  $\text{AgNO}_3$ , as directed at par. 526, then test specially for the acids indicated by these reagents, and also for those of the 4th group.

551. *Preliminary examination for acids.*—By heating the substance with concentrated  $\text{H}_2\text{SO}_4$ , the presence or absence of *volatile inorganic acids* is at once ascertained, these acids either volatilizing undecomposed, or yielding volatile products of decomposition. For this purpose a small portion of the dry substance is heated in a test-tube (not to boiling), with three or four times its volume of concentrated  $\text{H}_2\text{SO}_4$ ; when, in the case of all acids which are either volatile without decomposition, or are decomposed by  $\text{H}_2\text{SO}_4$  at a high temperature, gases or vapors are evolved, the properties of which, in most cases, indicate the nature of the acids present. The following table exhibits the behavior of the salts of the volatile acids with concentrated  $\text{H}_2\text{SO}_4$ ;—

WITHOUT DECOMPOSITION.	WITH DECOMPOSITION.
CO <sub>2</sub> . Inodorous; causes a <i>precipitate</i> in lime water.	HI. Violet vapors of I, which color starch-paste <i>blue</i> .
SO <sub>2</sub> . Odor of burning S; turns a solution of K <sub>2</sub> CrO <sub>3</sub> <i>green</i> .	HBr. Red vapors of Br, which color starch-paste <i>orange</i> .
H <sub>2</sub> S. Odor of rotten eggs; turns paper moistened with a lead solution <i>brown</i> .	HCN. Disengages CO, which burns with a <i>blue flame</i> .
HCl. Irritating gas, which gives white fumes in contact with NH <sub>3</sub> .	CrO <sub>3</sub> . Evolves O, the solution becoming <i>brown</i> or <i>green</i> .
HF. Fuming gas, which corrodes glass.	HClO <sub>3</sub> . <i>Greenish-yellow</i> explosive gas.
HNO <sub>3</sub> . Colorless acid gas, sometimes having brownish tint from a portion of it being decomposed; on the addition of copper filings <i>red fumes</i> , which color starch paste and KI <i>blue</i> .	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> . Evolves CO <sub>2</sub> and CO.

552. It must be observed that the behavior of a mixture of salts when heated with H<sub>2</sub>SO<sub>4</sub> is often different to the behavior of the salts when heated separately with H<sub>2</sub>SO<sub>4</sub>; thus, for instance, a mixture of a nitrate and chloride, when heated with H<sub>2</sub>SO<sub>4</sub>, evolves Cl, and red nitrous fumes. Mercury and tin chlorides are decomposed with difficulty, if at all, by H<sub>2</sub>SO<sub>4</sub>.

553. Answers to the following exercises must be written out.

#### EXERCISES.

143. Describe the chemical reactions involved in the etching of glass.

144. How can small quantities of HClO<sub>3</sub> be recognized in the presence of HCl?

145. What is meant by stating that a water is hard? and describe Clarke's process for softening hard water.

146. What is the action of H<sub>2</sub>S and SO<sub>2</sub> on highly oxidized bodies? Illustrate your answer by diagrams showing the action of H<sub>2</sub>S on Fe<sub>2</sub>SO<sub>4</sub> and SO<sub>2</sub> on K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>.

147. What changes do NiC<sub>2</sub>O<sub>4</sub> and CoC<sub>2</sub>O<sub>4</sub> undergo when heated in close vessels?

148. What is the action of HCl and H<sub>2</sub>SO<sub>4</sub> on chromates? Illustrate your answer by diagrams.

149. How is iodine prepared on the manufacturing scale?

150. How is fluorine detected in the presence of silicates?

151. Describe the properties and some of the transformations of  $\text{H}_2\text{C}_2\text{O}_4$ .

152. How is  $\text{HCy}$  prepared? what transformations does it undergo in the presence of acids and alkalies? and give the different methods for ascertaining its presence.

153. What change do the neutral and acid chromates of the alkaline metals undergo on being heated?

154. What is the action of  $\text{HF}$  upon  $\text{SiO}_2$  in the presence of water?

155. Chrome iron ore in fine powder is mixed with chalk, and the mixture is heated to bright redness in a current of air in a reverberatory furnace for nine or ten hours, the mixture being frequently stirred; it is afterwards treated with water, the clear solution drawn off from the insoluble matter, and  $\text{H}_2\text{SO}_4$  is then added to the solution until it is slightly acid;  $\text{K}_2\text{CO}_3$  is then added, the mixture is afterwards filtered, and the solution is evaporated until crystals begin to form. What change does the chrome iron undergo in roasting? what is dissolved out of the roasted mass by the water? why is the  $\text{H}_2\text{SO}_4$  added? what change does the  $\text{K}_2\text{CO}_3$  effect? and, finally, what substance is it that crystallizes out?

156. What takes place when a mixture of  $\text{NaCl}$ ,  $\text{K}_2\text{CrO}_4$ ,  $\text{H}_2\text{SO}_4$  is submitted to distillation?

157. Acids which form insoluble lead salts are frequently separated from other acids and substances which are not precipitated by lead salts, by means of lead acetate or nitrate, and washing the precipitate to free it from the other impurities and the excess of the soluble lead salt added, afterwards suspending the insoluble lead salt in water, and passing  $\text{H}_2\text{S}$  through the mixture to excess; the lead is converted into insoluble  $\text{PbS}$ , whilst the acid remains in solution; could chromic acid be purified in this manner? Give reasons for the opinion expressed.

158. Describe the effect of heat on the following phosphates,  $\text{Na}_3\text{PO}_4$ ,  $\text{Na}_2\text{HPO}_4$ , and  $\text{NaH}_2\text{PO}_4$ .

159. Is there any method of disintegrating a silicate insoluble in acids without fusing it?

## ORGANIC ACIDS.

554. Organic acids cannot be detected with the same certainty and precision as the inorganic acids. To detect with

certainly even some of those which we have given requires on the part of the analyst great skill and judgment. The special properties of each of the acids are first described, their division into groups, with a description of the properties of each group of acids, and afterwards the processes to be followed in preparing solutions for their examination.

BEHAVIOR OF THE ACIDS AND THEIR RADICALS  
WITH REAGENTS.

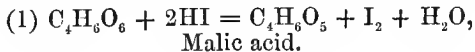
TARTARIC ACID,  $\text{H}_2\text{H}_2\text{C}_4\text{H}_2\text{O}_6 = \text{H}_2\bar{\text{T}}$ .

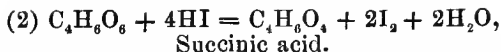
SOLUTION FOR THE REACTIONS,  $\text{NaHH}_3\text{C}_4\text{H}_2\text{O}_6$  in water.

555. This acid is tetratomic, but only *two of its four replaceable atoms of H can be replaced by metals*, the other two are replaceable by alcoholic and acid radicals. This acid forms with monatomic metals both acid and neutral salts, for example, hydric potassic tartrate  $\text{KHH}_3\text{C}_4\text{H}_2\text{O}_6$ , potassic tartrate  $\text{K}_2\text{H}_2\text{C}_4\text{H}_2\text{O}_6$ , potassic sodic tartrate (Rochelle salt)  $\text{KNaH}_2\text{C}_4\text{H}_2\text{O}_6$ ; with diatomic metals it forms neutral salts, having the general formula  $\text{M}''\text{H}_2\text{C}_4\text{H}_2\text{O}_6$ ; one of the commonest tartrates is the so-called tartar emetic  $\text{KSbOH}_2\text{C}_4\text{H}_2\text{O}_6$ , which may be considered as containing the monatomic radical  $\text{SbO}$  in place of an atom of  $\text{H}$ , or a monatomic metal.

556. This acid exists in grapes, tamarinds, and many other fruits; it is deposited during the fermentation of the grape juice as the acid potassic salt  $\text{KHH}_3\text{C}_4\text{H}_2\text{O}_6$ , this deposit is called in commerce crude *tartar*, or *argol*, and when purified by recrystallization, *cream of tartar*. The acid is obtained by precipitating from the tartar solution the calcic salt, and decomposing this salt with dilute  $\text{H}_2\text{SO}_4$ , and then evaporating the solution to the crystallizing point. It occurs in the form of colorless, transparent crystals: it dissolves in cold, as well as in hot water, and is soluble also in alcohol, the solution is acid to test-paper, and if kept for a short time, becomes mouldy and decomposes. It can be produced artificially by acting upon milk sugar with  $\text{HNO}_3$ ; it is also obtained by treating dibromosuccinic acid,  $\text{C}_4\text{H}_4\text{Br}_2\text{O}_4$ , with  $\text{Ag}_2\text{O}$ , in the presence of water, thus:  $\text{C}_4\text{H}_4\text{Br}_2\text{O}_4 + \text{Ag}_2\text{O} + \text{H}_2\text{O} = \text{C}_4\text{H}_6\text{O}_6 + 2\text{AgBr}$ .

By the action of  $\text{HI}$  or iodide of phosphorus, it is reduced to malic, or to succinic acid:—





In the presence of oxidizing agents it is converted (generally) into carbonic, formic, and oxalic acids. When fused with KHO the acid and tartrates break up into an acetate and an oxalate:  $\text{C}_4\text{H}_6\text{O}_6 + 3\text{KHO} = \text{KC}_2\text{H}_3\text{O}_2 + \text{K}_2\text{C}_2\text{O}_4 + 3\text{H}_2\text{O}$ .

557. The acid and its salts, when heated, char, and emit a peculiar and very characteristic odor, resembling that of burnt sugar, which is best perceived when the substance is heated in a tube open at both ends. If the acid, or a tartrate in the solid state, be heated with concentrated  $\text{H}_2\text{SO}_4$ , the mixture acquires a black or a brownish-black color, owing to the separation of carbon, which takes place simultaneously with the evolution of CO. If a solution of potassic permanganate be rendered strongly alkaline, and a tartrate be added and the solution boiled, the solution becomes decolorized, the permanganate being reduced to  $\text{MnO}_2$ .

558. The tartrates of the alkaline metals and of those of the 3d and 4th groups are soluble in water. The tartrates that are insoluble in water are soluble in HCl or  $\text{HNO}_3$ .

559. As tartaric acid is a test for K, so in like manner potassic salts, especially the acetate, can be employed as a test for tartaric acid, free and combined; for this purpose a concentrated solution of potassic acetate is added to the solution, and the mixture is then shaken very violently, as the precipitate is greatly promoted by shaking, and the addition of an equal volume of alcohol heightens the delicacy of the reaction.

560.  $\text{BaCl}_2$  produces in solutions of the tartrates a white precipitate of  $\text{BaH}_2\text{C}_4\text{H}_2\text{O}_6$ , which is soluble in solutions containing ammoniac salts and in HCl.

561.  $\text{CaCl}_2$  precipitates from solutions of the tartrates a white precipitate of  $\text{CaH}_2\text{C}_4\text{H}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$ , which is soluble in acetic and the mineral acids; ammoniac salts retard the formation of the precipitate. It is distinguished from calcic phosphate, calcic borate, and calcic oxalate, by dissolving in a cold not over-dilute solution of KHO, from which solution it is precipitated on boiling, and again redissolved as the liquid cools.

562. *Lime-water* produces in solutions of the tartrates and also in solutions of the acid, if added until the solution

is alkaline, a white flocculent precipitate of calcic tartrate, which becomes crystalline after some time; this precipitate is soluble in tartaric acid and in solution of  $\text{NH}_4\text{Cl}$ , from which solutions the calcic tartrate separates after some time in the crystalline form.

563. Plumbic acetate produces in solutions of tartaric acid and the tartrates a white precipitate of  $\text{PbH}_2\text{C}_4\text{H}_2\text{O}_6$ , which dissolves readily in  $\text{HNO}_3$ , in  $\text{NH}_4\text{HO}$ , in tartaric acid, and in ammoniac tartrate.

564.  $\text{AgNO}_3$  produces, in solutions of the *neutral* tartrates, a white precipitate of  $\text{Ag}_2\text{H}_2\text{C}_4\text{H}_2\text{O}_6$ , which is soluble in  $\text{NH}_4\text{HO}$ ; if the ammoniac solution be gently heated a bright metallic deposit of silver is formed.

### CITRIC ACID, $\text{H}_3\text{HC}_6\text{H}_4\text{O}_7$ .

*Solution for the reactions  $\text{Na}_3\text{HC}_6\text{H}_4\text{O}_7$  in water.*

565. This acid is tetratomic, but only three of its four replaceable atoms of H can be replaced by metals; the fourth is called alcoholic hydrogen. It forms with the alkali metals, one neutral and two acid salts, *ex.* tripotassic citrate  $\text{K}_3\text{HC}_6\text{H}_4\text{O}_7$ , hydric dipotassic citrate  $\text{K}_2\text{HHC}_6\text{H}_4\text{O}_7$ , and dihydric potassic citrate  $\text{KH}_2\text{HC}_6\text{H}_4\text{O}_7$ ; it forms with dyad metals two classes of salts having the following general formulæ:  $\text{M}''\text{HHC}_6\text{H}_4\text{O}_7$  and  $\text{M}''_3(\text{HC}_6\text{H}_4\text{O}_7)_2$ .

566. This acid exists in lemons, oranges, citrons, gooseberries and many other fruits; it is prepared from lemon juice by neutralizing it with chalk, after it has fermented a little to separate the mucilage and other impurities; the lime salt thus obtained is decomposed with dilute  $\text{H}_2\text{SO}_4$ , and the solution evaporated to the crystallizing point. It forms large transparent crystals, it is very soluble in hot and cold water, and also in alcohol; its solution is acid to test-paper, and decomposes on keeping. Fused with KHO it gives potassic acetate and oxalate —  $\text{C}_6\text{H}_8\text{O}_7 + 4\text{KHO} = 2\text{KC}_2\text{H}_3\text{O}_2 + \text{K}_2\text{C}_2\text{O}_4 + 3\text{H}_2\text{O}$ .

567. Citric acid chars when heated; the charring is attended with an evolution of pungent fumes which cannot be mistaken for those evolved by tartaric acid. If the acid or a citrate in the solid state be heated with concentrated  $\text{H}_2\text{SO}_4$ , CO, and  $\text{CO}_2$  are evolved without any change of color in the liquid; the mixture blackens only after long boiling. If a solution of potassic permanganate be rendered strongly alkaline, and a salt of citric acid be added

and the mixture boiled, the solution gradually becomes green, and so remains on continued boiling.

568. Both the neutral and acid salts of the alkaline citrates are readily soluble in water; citric acid is not, therefore, precipitated from its solutions on the addition of potassic acetate. Citric acid, like tartaric acid, prevents the precipitation of alumina, ferric oxide, and other bases, by the alkalies.

569. A solution of  $\text{BaCl}_2$  produces in solutions of the citrates a white precipitate of baric citrate, which is soluble in much water, in free acids, and in solutions of ammoniac salts.

570. A solution of  $\text{CaCl}_2$  produces in solutions of citrates, but not in citric acid, a precipitate of calcic citrate, which is more insoluble in hot water than cold, insoluble in  $\text{KHO}$ , soluble in a cold solution of  $\text{NH}_4\text{Cl}$ , from which it is precipitated on boiling the solution. Free citric acid must be neutralized by  $\text{KHO}$  or  $\text{NaHO}$  before adding  $\text{CaCl}_2$  to its solution.

471. Lime-water produces no precipitate in cold solutions of citric acids or the citrates; but on boiling the solution a precipitate is produced, which redissolves almost entirely when the liquid becomes cold.

572. If a solution of ferric tartrate is evaporated on the water-bath to a syrupy consistence, a solid basic salt is deposited, but ferric citrate under the same circumstances deposits no solid salt. Upon this difference of deportment of the ferric salts of the two acids has been based a method for the detection of tartaric acid in citric acid; by this method even minute quantities of tartaric acid admit of being detected in citric acid; the following is the method: the citric acid to be examined is dissolved in water, hydrate of ferric oxide is added to the solution in excess and the mixture is heated to about  $90^\circ \text{C}$ . When the acid has become saturated with oxide, the iron is filtered off from the undissolved portion; the solution is then evaporated on the water-bath to a syrupy consistence; if the citric acid contained tartaric acid, there would be formed a deposit of an insoluble basic ferric tartrate; if, on the contrary, the citric acid is pure, there is no deposit from the syrupy liquid, it remains perfectly clear.

573. A solution of plumbic acetate, when added in excess, produces in solution of citric acid a white precipitate of  $\text{PbHHC}_6\text{H}_4\text{O}_7 \cdot \text{H}_2\text{O}$ , which, when washed, dissolves readily in ammonia.



574. Tartaric and citric acids are largely used by calico printers as discharges in the production of white spots on a colored ground.

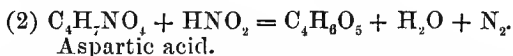
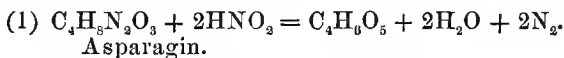
### MALIC ACID, $\text{H}_2\text{C}_4\text{H}_4\text{O}_5$ .

*Solution for the reactions,  $\text{Na}_2\text{C}_4\text{H}_4\text{O}_5$ .*

575. This acid contains only two atoms of H replaceable by metals, although it is, probably, a triatomic acid. It forms with the alkaline metals a neutral and an acid salt; it forms, also, with calcium and other diatomic metals, an acid as well as a neutral salt. Nearly all the malates are soluble in water. It is the acid of apples, pears, and various other fruits. It crystallizes with great difficulty, it is deliquescent, and is soluble in alcohol as well as water; its solution is acid to test-paper, and becomes mouldy and decomposes by keeping. It can be produced artificially by the action of moist  $\text{Ag}_2\text{O}$  on monobromosuccinic acid.



It is also produced by the action of nitrous acid on asparagin, and on aspartic acid.



By the action of HI it is converted into succinic acid— $\text{C}_4\text{H}_6\text{O}_5 + 2\text{HI} = \text{C}_4\text{H}_6\text{O}_4 + \text{H}_2\text{O} + \text{I}_2$ . If kept at a temperature of  $150^\circ \text{C}$ ., it is slowly resolved into water and fumaric acid ( $\text{C}_4\text{H}_4\text{O}_4$ ); if kept for some hours between  $175^\circ$  and  $180^\circ$ , it is resolved into water, fumaric acid, and maleic acid, an acid isomeric with fumaric acid. Fused with KHO it splits up like tartaric and citric acids into oxalic and acetic acids. Concentrated  $\text{H}_2\text{SO}_4$  decomposes the acid and the malates in the solid state with evolution of CO; the mixture blackens only after long boiling.

576. A solution of  $\text{CaCl}_2$  does not produce a precipitate in solutions of the free acid or its salts until alcohol is added.

577. "Lime-water produces no precipitate in solutions of free malic acid, nor in solutions of malates. The fluid

remains perfectly clear even upon boiling, provided the lime-water is prepared with boiling-water."

578. A solution of lead acetate throws down, from a solution of the acid or its salts, a white precipitate of  $\text{PbC}_4\text{H}_4\text{O}_6 \cdot 3\text{H}_2\text{O}$ . If the fluid in which the precipitate is suspended is boiled, the precipitate fuses to a mass resembling resin melted under water. But this reaction is only distinctly marked when the plumbic malate is tolerably pure; if mixed with other lead salts, it does not present this appearance, or at least imperfectly.

### BENZOIC ACID, $\text{HC}_7\text{H}_5\text{O}_2$ .

*Solution for the reactions,  $\text{NH}_4\text{C}_7\text{H}_5\text{O}_2$ , in water.*

579. This acid is monatomic. It is contained in gum benzoin. The pure acid appears under the form of white scales or needles, or simply as a crystalline powder. It is readily dissolved by alcohol and ether; it is only slightly soluble in cold water; on the addition of  $\text{HCl}$  to an aqueous solution of any of its salts, it separates from the solution as a white crystalline powder. It volatilizes completely when heated, with partial decomposition, the fumes cause a peculiar irritating sensation, and provoke coughing. When heated in a tube open at both ends, a portion of the acid condenses upon the cool part of the tube. When heated with concentrated  $\text{H}_2\text{SO}_4$  it volatilizes without carbonizing.

580. It can be produced artificially by oxidizing bitter almond oil, or by boiling hippuric acid with  $\text{HCl}$ , or by oxidizing benzilic alcohol.

581.  $\text{BaCl}_2$  and  $\text{CaCl}_2$  do not precipitate this acid under any circumstances.

582.  $\text{Fe}_2\text{Cl}_6$  produces in neutral solutions of this acid a precipitate of ferric benzoate, the color of which is pale buff;  $\text{NH}_4\text{HO}$  in excess withdraws the acid from this precipitate,  $\text{Fe}_2\text{H}_6\text{O}_6$  remaining. Ferric benzoate differs from ferric succinate in this—that it dissolves in a little  $\text{HCl}$  with separation of the greater portion of the benzoic acid.

### SUCCINIC ACID, $\text{H}_4\text{C}_4\text{H}_4\text{O}_4$ .

*Solution for the reactions,  $(\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_4$ , in water.*

583. This acid is bibasic, it therefore forms an acid and a neutral salt with the alkaline metals. It occurs ready formed in amber and in certain lignites. It is crystalline

and melts at  $180^{\circ}$ , but begins to emit suffocating vapors below its melting point; it does not carbonize when heated. It is more soluble in hot than cold water; it is less soluble in alcohol, and nearly insoluble in ether. Fused with KHO it yields a carbonate and an oxalate, together with a gaseous hydrocarbon. It offers great resistance to the action of oxidizing agents; in fact it is a frequent product of the oxidation of organic substances, especially fats. It is also formed in many processes of fermentation, and we have already noticed that it is produced from malic and tartaric acids, by acting on them with HI. It is not attacked by concentrated  $\text{H}_2\text{SO}_4$ , even when heated.

584. The succinates of the alkali metals and of magnesium are easily soluble in water; those of the alkaline earth metals, and most other diatomic metals, are sparingly soluble; those of the sesqui-atomic metals are insoluble.

585.  $\text{BaCl}_2$  after the addition of  $\text{NH}_4\text{HO}$  and alcohol, precipitates this acid from its solutions in the form of  $\text{BaC}_4\text{H}_4\text{O}_4$ , benzoic acid does not exhibit this reaction; succinic acid is further distinguished from benzoic acid by not being precipitated from its soluble salts by the mineral acids.

586.  $\text{Fe}_2\text{Cl}_6$  produces, in neutral solutions of the succinates, a precipitate of the ferric succinate, the color of which is reddish-brown. It is decomposed in the same manner as ferric benzoate by  $\text{NH}_4\text{HO}$ .

#### TANNIC ACID (Tannin) $\text{H}_3\text{C}_{27}\text{H}_{19}\text{O}_{17}$ .

*Solution for the reactions, the acid in water.*

587. This acid is a solid body, of a light straw color, and not crystalline. It is very soluble in water; the solution absorbs oxygen from the air, which converts the acid into two others, gallic and ellagic. It is precipitated from concentrated solutions by dilute  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$ , in the form of a paste. It is also precipitated by dilute starch-paste, by gelatine, and albumen. It is completely removed from its solutions by placing in the liquid a piece of animal membrane.

588.  $\text{Fe}_2\text{Cl}_6$  produces, in solutions of tannic acid or tannates, a dark blackish-blue precipitate.

589. Tartar emetic gives in solutions of this acid a white gelatinous precipitate.

590. Concentrated  $\text{H}_2\text{SO}_4$ , treated with the acid or the

tannates in the solid state, produces a dark purplish-black liquid immediately, but does not evolve CO.

### GALLIC ACID, $\text{H}_3\text{C}_7\text{H}_3\text{O}_5$ .

*Solution for the reactions, the acid in water.*

591. This acid is tribasic, it therefore forms with the monatomic metals three series of salts. It is contained in green and black tea, and in many other plants. It can be produced artificially by the action of acids or alkalis on tannic acid. It crystallizes in prisms of a silky lustre, of a very pale yellow color. It is not very soluble in cold water, but dissolves in three parts of boiling water. Its alkaline solutions, when exposed to the air, become first yellow, then green, red, brown, and finally nearly black, owing to the absorption of oxygen. It is not precipitated by gelatine or animal membrane. By this behavior it may be distinguished and separated from tannic acid.

592.  $\text{Fe}_2\text{Cl}_6$  produces, in solutions of this acid and its salts, a bluish-black color.

593. Concentrated  $\text{H}_2\text{SO}_4$  behaves with gallic acid much in the same way as with tannic acid.

### ACETIC ACID, $\text{HC}_2\text{H}_3\text{O}_2$ .

*Solution for the reactions,  $\text{NaC}_2\text{H}_3\text{O}_2$ , in water.*

594. This acid, so well known under the name of vinegar, is monobasic; the normal salts are all soluble in water; the normal acetates of the alkali metals can combine with a molecule of acid as they do with water. These salts are called diacetates. Some normal salts in the same way can combine with a molecule of a metallic oxide or its hydrate, and form basic salts. Solutions of ferric and aluminic acetates are decomposed by boiling into basic salts and free acid which is expelled; these salts experience the same decomposition, if a cotton cloth is immersed in their solutions and hung up in a moist and warm atmosphere; this process is called *ageing* by the cotton-printers, and the deposit of the basic salts in the cloth is called a mordant, the commercial names of ferric and aluminic acetate solutions are *iron liquor* and *red liquor*.

595. Acetic acid exists in the juices of many plants, especially of trees. It is formed in the destructive distillation of organic substances, especially of wood. The greater part of the acid used in the arts is obtained from this source,

and goes under the name of *wood vinegar*, or pyroligneous acid. Alcohol is converted into acetic acid by various processes of oxidation; in the ordinary processes for making vinegar, either from wine or malt, an alcoholic solution is exposed to the joint influence of air and a ferment. Acetates are formed by heating cyanide of methyl ( $\text{CH}_3\text{CN}$ ) with the caustic alkalies, and by acting on sodium-methyl ( $\text{CH}_3\text{Na}$ ) with  $\text{CO}_2$ , and by other processes.

596. It is a colorless crystalline solid below  $16^\circ \text{C}$ ., above that temperature it is a thin colorless liquid of an exceedingly pungent and well-known odor of vinegar. It is miscible in all proportions with water, alcohol, and ether, and dissolves camphor and several resins. In the liquid state it has a density of 1.063, and boils at  $120^\circ \text{C}$ .; its vapor is inflammable. On account of its solidifying below  $16^\circ$ , it has received the name of *glacial acetic acid*, in contra-distinction to the mixtures of water and the acid which do not crystallize; it is to these mixtures that the name acetic acid is commonly applied.

597. If  $\text{Fe}_2\text{Cl}_6$  is added to acetic acid, and the acid is then nearly saturated with  $\text{NH}_4\text{HO}$ , or if a neutral acetate is mixed with  $\text{Fe}_2\text{Cl}_6$ , the fluid acquires a deep dark-red color, owing to the formation of ferric acetate. By boiling, the fluid becomes colorless if it contains an excess of acetate, the whole of the Fe precipitating as a basic acetate, in the form of brown-yellow flakes.  $\text{NH}_4\text{HO}$  precipitates from it the whole of the Fe as  $\text{Fe}_2\text{H}_6\text{O}_6$ . By addition of  $\text{HCl}$  a fluid which is red from the presence of ferric acetate turns yellow (difference from ferric sulphocyanide).

598. Acetic acid or acetates when heated with  $\text{HgCl}_2$  produce no precipitate of  $\text{HgCl}$ .

599. When  $\text{H}_2\text{SO}_4$  is added to acetates, the acetic acid is liberated, and is recognized by its odor of vinegar. If the acetate is distilled with the  $\text{H}_2\text{SO}_4$ , the acetic acid is obtained in the distillate.

600. When acetates are heated with about equal volumes of concentrated  $\text{H}_2\text{SO}_4$  and alcohol, acetic ether ( $\text{C}_2\text{H}_5\text{C}_2\text{H}_3\text{O}_2$ ) is formed, which is readily distinguished by its characteristic odor.

601. Concentrated  $\text{H}_2\text{SO}_4$  occasions no blackening when heated with acetic acid or its salts.

602. If an excess of  $\text{PbO}$  be digested in acetic acid, there is formed a soluble basic lead acetate, which has an alkaline reaction.

FORMIC ACID,  $\text{HCHO}_2$ .

*Solution for the reactions,  $\text{NaCHO}_2$  in water.*

603. This acid is monobasic; all its salts are soluble in water; it occurs in ants, in caterpillars, and in several secretions of the human body; it is present in the juice of the stinging-nettle and other vegetables; it has been found in some mineral waters. It may be prepared by passing  $\text{CO}$  over moist  $\text{KHO}$ , and by passing  $\text{CO}_2$  and aqueous vapor over  $\text{K}$  at a moderate heat,  $\text{KHCO}_3$  being formed at the same time; it is also formed by acting on  $\text{HCN}$  with an alcoholic solution of  $\text{KHO}$ ; and by distilling dry oxalic acid mixed with glycerin, which takes no part in the decomposition, but appears to act by preventing the temperature rising too high; it is formed by the partial oxidation of a great variety of organic bodies, as starch, gum, tartaric acid, etc.

604. This acid is a clear colorless liquid which fumes slightly in the air; it has an exceedingly penetrating odor; it boils at  $101.1^\circ \text{C.}$ , and crystallizes in large brilliant plates when cooled below  $-1^\circ \text{C.}$  Its sp. gr. is 1.235, and it mixes with water and alcohol in all proportions. When exposed to the action of heat, it volatilizes completely; the vapor is inflammable and burns with a blue flame.

605. The formates are all decomposed by heat; the formates of the alkalies and alkaline earth metals ignited out of contact with air leave carbonates slightly blackened by charcoal,  $\text{CO}$  and  $\text{H}$  being evolved;\* the formates of other metals (copper and lead for example) when heated give off  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ , the metal being left in the metallic state.  $\text{NH}_4\text{CHO}_2$  when exposed to a high temperature is decomposed into  $\text{HCN}$  and  $\text{H}_2\text{O}$ .

606. If  $\text{Fe}_2\text{Cl}_6$  is added to a neutral formate, the fluid acquires a blood-red color; the liquid becomes colorless on boiling if an excess of the formate be present, all the iron being precipitated in the form of a basic salt. The formates, in fact, exactly resemble the acetates in their behavior with ferric salts.

607. This acid is a powerful reducing agent; it reduces the oxides of the noble metals, yielding  $\text{H}_2\text{O}$  and  $\text{CO}_2$ ; by heating it with a solution of  $\text{AgNO}_3$ , the  $\text{Ag}$  is deposited sometimes in the pulverulent state and sometimes as a

\* Baric formate yields the products above mentioned, together with gaseous hydrocarbons, viz. marsh-gas, ethylene, and tritylene.

specular coating on the glass tube; this reaction distinguishes it from acetic acid, which does not reduce the silver nitrate.

608. If the acid or an alkaline formate is heated to from  $60^{\circ}$  to  $70^{\circ}$  C. with  $\text{HgCl}_2$ ,  $\text{HgCl}$  precipitates. If the mixture is heated to  $100^{\circ}$  C.,  $\text{Hg}$  separates along with  $\text{HgCl}$ .

609. When dilute  $\text{H}_2\text{SO}_4$  is added to formates the acid is liberated and is recognizable by its odor; if the formiate is distilled with the  $\text{H}_2\text{SO}_4$ , the formic acid is obtained in the distillate.

610. Upon heating a formate with a mixture of  $\text{H}_2\text{SO}_4$  and alcohol, formic ether ( $\text{C}_2\text{H}_5\text{CHO}_2$ ) is produced, which has an agreeable odor resembling peach kernels.

611. Concentrated  $\text{H}_2\text{SCl}_4$ , when heated with formic acid or a formate, decomposes the acid into  $\text{CO}$  and  $\text{H}_2\text{O}$ ; there is therefore no blackening, however long the heat may be continued.

#### URIC ACID, $\text{H}_2\text{C}_5\text{N}_4\text{H}_2\text{O}_3$ .

*Solution for the reactions, the acid.*

612. This acid is bibasic; it therefore forms two series of salts with the monatomic metals, viz., neutral salts and acid salts. "It is a product of the incomplete oxidation of animal tissues. In combination chiefly with ammonia it forms the principal urinary constituent voided by insects, land-reptiles, and birds (whence it is found in guano). Normally it occurs but in small proportion in the urine of man, and is found in yet smaller proportions in that of carnivorous quadrupeds, and can scarcely be said to exist in that of herbivorous and omnivorous quadrupeds." The solid white excrement of serpents consists almost entirely of uric acid and ammonic urate. This acid has never yet been formed by artificial means.

613. This acid occurs in delicate white needles; it is scarcely soluble in cold water, dilute  $\text{HCl}$  or  $\text{HC}_2\text{H}_3\text{O}_2$ ; it is soluble in alcohol and ether. It dissolves in concentrated  $\text{H}_2\text{SO}_4$  without apparent decomposition, and is precipitated by dilution with water. It is soluble in the alkalies and alkaline salts, from which solutions it is precipitated on the addition of acids.

614. Urates, with the exception of the *potassic* and *sodic* ones, are almost all insoluble in water; the ammonic salt is

extremely insoluble in water; it is however dissolved by NaCl or  $\text{Na}_2\text{HPO}_4$ , sodic urate being formed.

615. The CALCIUM SALT is white; the FERRIC SALT brown; the COPPER SALT green; the SILVER SALT white, rapidly becoming black if the liquid be heated; the MERCURY and LEAD SALTS are white.

616. Uric acid yields by destructive distillation cyanic, hydrocyanic, and carbonic acids, ammoniac carbonate, and a black coaly residue rich in nitrogen. By fusion with KHO it furnishes carbonate cyanate and cyanide of the alkaline metal.

617. It dissolves with the aid of heat in dilute  $\text{HNO}_3$ ; the solution is attended with effervescence and evolution of red fumes, the uric acid being oxidized at the expense of the  $\text{HNO}_3$ . If the  $\text{HNO}_3$  solution be evaporated in a porcelain dish on the water-bath just to dryness, and a glass stopper moistened with strong ammonia-water be then held over the residue in the dish, a *magnificent purple color* is produced, owing to the formation of MUREXIDE ( $\text{C}_8\text{N}_6\text{H}_8\text{O}_6$ ).

618. If uric acid be dissolved in sodic carbonate, and a drop of the solution be laid on paper moistened with silver solution, a *brown spot* is formed, argentic carbonate being reduced by uric acid at ordinary temperatures.

619. Concentrated  $\text{H}_2\text{SO}_4$  dissolves uric acid, with the aid of heat, without change; if the heat be long continued, the liquid becomes dark.

#### CLASSIFICATION OF THE ORGANIC ACIDS, WITH A DESCRIPTION OF THE PROCESSES TO BE FOLLOWED IN THE EXAMINATION OF SUBSTANCES FOR THESE ACIDS.

*Classification of the acids.*—The organic acids described in this part (Part I.) of this book may be conveniently divided into four groups, as follows:—

##### FIRST GROUP.

620. 1st Division.—Acid which is precipitated from *neutral* solutions in the cold by  $\text{CaCl}_2$ , TARTARIC ACID; the properties of calcic tartrate are given in par. 561. 2d Division.—Acid which is precipitated by  $\text{CaCl}_2$  from boiling solutions rendered alkaline by lime-water, CITRIC ACID. 3d Division.—Acid which is not precipitated from hot or cold solutions by  $\text{CaCl}_2$ , but its calcic salt is precipitated on adding alcohol to the solution, MALIC ACID.



Oxalic, boracic, phosphoric, hydrofluoric, carbonic, arsenious, and arsenic acids are also precipitated from neutral solutions by  $\text{CaCl}_2$ .

### SECOND GROUP.

621. *1st Division.*—Acids which give precipitates in *neutral* solutions with  $\text{Fe}_2\text{Cl}_6$ , TANNIC, BENZOIC, and SUCCINIC ACIDS. Tannic acid gives a precipitate with  $\text{Fe}_2\text{Cl}_6$  in acid, as well as neutral solutions. The iron salt does not precipitate benzoic and succinic acids in the presence of a citrate.

2d.—Acids which give a coloration in *neutral* solutions with  $\text{Fe}_2\text{Cl}_6$ , ACETIC, FORMIC, and GALLIC ACIDS; the two former give a reddish and the latter a black coloration.

PHOSPHORIC, ARSENIC, and BORACIC ACIDS give precipitates in *neutral* solutions with  $\text{Fe}_2\text{Cl}_6$ , the first two in acid as well as neutral solutions.

### THIRD GROUP.

622. Acids which are precipitated from neutral solutions by  $\text{AgNO}_3$ . TARTARIC, CITRIC, MALIC, BENZOIC, SUCCINIC, AND FORMIC ACIDS. Argentic tartarate, and argentic formate are reduced on being heated, Ag separating.

### FOURTH GROUP.

*Acetic acid, uric acid.*

623. These acids are not precipitated by the group reagents, nor do they give any peculiar coloration with them.

### DETECTION OF THE ORGANIC ACIDS.

624. TARTARIC ACID.—The peculiar and highly characteristic odor which this acid evolves on ignition (557), prevents it from being overlooked if present in any quantity. But the test with acetate of potash (559) ought to be made in all cases; the solution to be examined for tartaric acid must be neutral, or if acid the free acid must only be acetic acid or tartaric acid. For detecting minute quantities of tartaric acid in the presence of citric acid, employ the method described in par. 572.

625. CITRIC ACID.—Oxalic and tartaric acids, if present, require to be removed before examining for this acid, add, therefore, to the solution in *the cold*  $\text{CaCl}_2$  and lime-water

to alkaline reaction; calcic tartrate and oxalate will be precipitated,\* filter and heat the filtrate to boiling. Calcic citrate will precipitate; filter and examine the filtrate for malic acid as directed in next par.

626. MALIC ACID.—To the filtrate from the calcic citrate precipitate, is added alcohol, calcic malate will precipitate if that acid be present. Malic acid is further distinguished from tartaric and citric acids, by not being blackened when heated with concentrated  $H_2SO_4$ .

627. BENZOIC ACID.—This acid, in the presence of succinic acid, is best detected by treating the iron precipitate of the two acids, after it has been washed, with  $NH_4HO$ , and then filtering, and after concentrating the filtrate dividing it into two parts, mixing one part with  $HCl$ , when benzoic acid, if present, will be precipitated; in the other part, succinic acid is examined for by adding  $BaCl_2$  and alcohol (585).

628. SUCCINIC ACID.—This acid is best detected in the presence of benzoic acid, by the method described in the previous paragraph. The student must remember what has been stated in the 2d group of acids that  $Fe_2Cl_6$  does not precipitate these two acids in the presence of alkaline citrates.

629. TANNIC ACID.—This acid is best detected in the presence of gallic acid, by the method described at 587.

630. GALLIC ACID.—This acid is best detected in the presence of tannic acid, by the method described at 591.

631. ACETIC ACID.—This acid is best detected by the methods described at 597 and 600.

632. FORMIC ACID.—This acid is best detected by the methods described at 607, 608, and 611.

633. URIC ACID.—This acid is best detected by the method described at 617 and 618.

634. PREPARATION OF THE SOLUTION.—When the substance under examination is soluble in water, or if it is in solution and the fluid is water, it requires a little preparation before it can be examined with advantage for the organic acids, as it conduces much to the success of the examination if no other metals but the alkaline ones are present. In order to remove the other metals, the solution has sometimes to be treated with  $H_2S$ , and  $(NH_4)_2S$ ; but

\* The separation of calcic tartrate is promoted by agitation. Calcic tartrate is separated from calcic oxalate by treating the precipitate with solution of  $KHO$  (561).

generally it is only necessary to boil the solution with a slight excess of  $\text{Na}_2\text{CO}_3$ ; by this reagent the majority of the metals, especially if citric acid is absent, except the alkaline ones, are removed. After the solution has been boiled for some time it is filtered, and to the filtrate is added  $\text{HNO}_3$ , very slightly in excess; the solution is then gently heated in order to expel the  $\text{CO}_2$ . After this,  $\text{NH}_4\text{HO}$  is added in very slight excess; and when it is required to have the solution perfectly neutral, as in testing with  $\text{AgNO}_3$ , and  $\text{Fe}_2\text{Cl}_6$ ; the solution, which has been rendered slightly alkaline with  $\text{NH}_4\text{HO}$ , is boiled in an evaporating dish until it is neutral to test-paper. When ammoniac salts are present in the substance under examination, the solution must, even if no other metals but the alkaline ones are present, be boiled with  $\text{Na}_2\text{CO}_3$  until all the  $\text{NH}_4\text{HO}$  is expelled, and the solution is then rendered neutral in the way just stated.

635. When  $\text{Na}_2\text{CO}_3$  fails to precipitate the metals, as it will frequently when the organic acid is *non-volatile*, especially if it be citric acid, add to the solution neutral lead acetate in excess, collect the precipitate and wash it thoroughly, then suspend it in water and pass  $\text{H}_2\text{S}$  through the mixture to excess, filter off from the  $\text{PbS}$ , and after expelling the excess of  $\text{H}_2\text{S}$  from the filtrate by heating it, neutralize exactly with  $\text{Na}_2\text{CO}_3$ , and then examine for the acids.

636. It is frequently advisable to separate the volatile acids, for this purpose the solution must be treated, if not acid already, with dilute  $\text{H}_2\text{SO}_4$ , and then distilled in a small retort, the liquid in the retort must be heated gently, not to boiling, and the distillate must be collected; the distillate may contain the following acids:  $\text{HCy}$ ,  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ ,  $\text{HNO}_3$ ,  $\text{HCHO}$ ,  $\text{HC}_2\text{H}_3\text{O}_2$ ,  $\text{H}_2\text{C}_4\text{H}_4\text{O}_4$ , and  $\text{HC}_7\text{H}_5\text{O}$ .

637. *Preliminary examination for organic acids.*—Heat a portion of the dry solid in a test-tube, with 3 or 4 times its volume of concentrated  $\text{H}_2\text{SO}_4$ , the organic acids treated of in this part of the book show the following behavior: Tartaric, tannic, and gallic acids are immediately blackened;  $\text{CO}_2$  is evolved at the same time from tartaric, but not from the other two acids. Citric, malic, and uric acids are not blackened unless boiled with the  $\text{H}_2\text{SO}_4$ , for some time, citric acid evolves  $\text{CO}$ , and  $\text{CO}_2$ , and malic acid,  $\text{CO}$ , on being acted on by  $\text{H}_2\text{SO}_4$ . Benzoic, succinic, and acetic acids are not blackened under any circumstances by  $\text{H}_2\text{SO}_4$ , but they volatilize in an unchanged state. Formic acid is

decomposed on being heated with  $\text{H}_2\text{SO}_4$  into  $\text{CO}$  and  $\text{H}_2\text{O}$  without any blackening.

638. Answers to the following exercises must be written out.

### EXERCISES.

160. What is the source of tartaric acid, and how is the acid obtained in the free state?

161. How is succinic acid distinguished from benzoic acid?

162. How can formic acid be obtained from inorganic sources, and what is the action of concentrated  $\text{H}_2\text{SO}_4$  upon it?

163. Give the formula for tartar, Rochelle salt, argol, tartar emetic, and cream of tartar.

164. A crystalline powder, representing a sample of organic acid, is given to you, and you are asked to say whether it is tartaric, citric, or oxalic acid. What tests would you apply for the solution of this problem?

165. How is succinic acid converted into malic and tartaric acids, and how is tartaric acid reconverted into malic and succinic acid?

166. How would you distinguish a tartrate from an oxalate and a citrate respectively?

167. Describe some methods for the manufacture of citric acid, and state some of its applications.

168. Malic acid is extracted from the juice of the mountain-ash berries; there are present along with it small quantities of tartaric and citric acids. The following method is followed for its extraction. Explain the different parts of the process. The juice, after being filtered, is *partly* neutralized with  $\text{K}_2\text{CO}_3$ , but the solution must still redden litmus pretty strongly, solution of  $\text{Pb}(\text{NO}_3)_2$ , or  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , is then added in excess, a curdy precipitate is formed, the mixture is then set aside for some days; with the exception of the mucous flocculent compound of lead and coloring matter, the precipitate by standing becomes converted into small needles; these are carefully freed from the coloring precipitate and other impurities by washing, they are then boiled in a quantity of dilute  $\text{H}_2\text{SO}_4$  not sufficient to decompose the whole of them, as long as any granular deposit continues to subside: to the mixture is then added an aqueous solution of  $\text{BaS}$ , until a filtered sample is found to contain  $\text{Ba}$ ; the liquid is then

filtered and the filtrate is boiled with an excess of  $\text{BaCO}_3$ ; the mixture is again filtered, and the Ba is precipitated from the filtrate by the careful addition of dilute  $\text{H}_2\text{SO}_4$ ; the liquid is again filtered and the filtrate evaporated to the crystallizing point.

169. From the properties and reactions which have been given of oxalic, tartaric, citric, and malic acid, devise another method which, from its cheapness and simplicity, would be suitable as a manufacturing process for the extraction of malic acid from vegetable juice, containing small quantities of oxalic, tartaric, and citric acids.

## EXAMINATION OF LIQUIDS AND SOLIDS.

### EXAMINATION OF A LIQUID.

639. The student, after he has passed through the different groups of bases and acids, in the manner previously described, commences the analysis of liquids, in which he has to look for all these bases and acids, with the exception of the organic acids.\*

640. Before commencing the actual analysis, it is necessary to ascertain by preliminary experiments—1. Whether there is *any solid substance* in solution. 2. Whether the solution is *neutral, acid, or alkaline*.

641. 1st. *To ascertain whether there is any solid substance in solution*.—Evaporate, by a gentle heat, a portion of the liquid to dryness, on platinum-foil. If no residue remain, it is probably pure water, which will be further confirmed if it has no action upon test-paper. If a residue remain, which is completely volatilized when the temperature is increased, the only basic substances which can be present are  $\text{NH}_3$ , Hg, As, and Sb. If the residue is not volatile, or at least not completely so, other substances besides these

\* The student will find it conducive to his success in many respects, if he does not engage in the detection of organic acids until he enters upon the examination of solid substances. He will, of course, in *practice*, have always first to ascertain whether organic substances are really present or absent in a solution, before he commences the actual analysis, as the presence of fixed organic matter prevents the detection of many inorganic substances; he will, likewise, in *practice*, have frequently to separate, by distillation, the liquid from the solid portion of a solution, in order to be perfectly certain that the fluid is *water*, and not any other liquid. This he will ascertain by examining the distilled fluid by the smell, taste, boiling point, specific gravity, etc.

must be present. In both cases it is requisite to perform the next experiment.

642. 2d. The solution is examined by well-prepared test-papers, as to its neutrality, etc. Each of the three cases which may occur, and the conclusions to which they lead, are considered in pars. 643, 645, 646.

643. The solution is *neutral*. A large number of substances must therefore be absent, because the soluble neutral salts of the greater proportion of the metals possess an acid reaction. The only salts which are neutral to test-papers are the soluble salts of silver and manganese, and some of the soluble salts of the alkalies and alkaline earth metals; some of the salts of these metals are therefore the only ones which can be present; but to distinguish still further, add to a portion of the solution  $(\text{NH}_4)_2\text{S}$ , if no precipitate is formed, Ag and Mn are absent, add then to the solution  $\text{Na}_2\text{CO}_3$  and boil, if this produces no precipitate the metals of the alkaline earths are absent; the only metals therefore which can be present are the alkaline metals. If  $(\text{NH}_4)_2\text{S}$  produces no precipitate, but a precipitate is produced by the  $\text{Na}_2\text{CO}_3$ , the alkaline earths and the alkaline metals have to be sought for, and if both reagents produce a precipitate, the one by  $(\text{NH}_4)_2\text{S}$  being *black*, then all the metals whose salts are *neutral* to test-paper must be sought for. Add HCl in the first instance, filter off from the insoluble AgCl, and add to the filtrate  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{HO}$ , and  $(\text{NH}_4)_2\text{S}$ ; if a precipitate is produced filter and examine the filtrate for the members of the 2d and 1st groups in the usual manner.

644. *Examination for the acids*.—Very few acid radicals can be present if Ba, Mn, or Ag are present, as so many of their salts are insoluble in water, and some of the baric salts which are soluble in water are alkaline to test-paper; and if K, Na, and  $\text{NH}_4$  are the only basic radicals that are present, a large number of acid radicals must be absent, as so many of the alkaline salts are alkaline to test-paper; add to separate portions of solution  $\text{BaCl}_2$  and  $\text{AgNO}_3$ , according to par 550.

645. The solution is *acid*. The acidity may proceed from the presence of a free acid, an acid salt, or a neutral salt having an acid reaction. To ascertain to which of these causes the acidity is due, place the end of a glass rod moistened with a solution of  $\text{Na}_2\text{CO}_3$ , into a portion of the fluid in a watch-glass. If the solution becomes turbid and remains so, it is due to the presence of a neutral salt;

if it becomes clear again, the reaction is due either to an acid salt or a free acid. Carbonates and sulphides cannot be present in an acid solution. Examine for the basic constituents in the usual manner. Examine for the acids according to par. 546 if it is a neutral salt having an acid reaction; if an acid salt or a free acid is present, examine according to par. 547.

646. The solution is *alkaline*. The alkalinity may proceed from an alkaline carbonate, silicate, borate, or phosphate; or it may arise from the presence of a free alkali or alkaline earth, or from the cyanogen and sulphur compounds of these metals. If the alkalinity proceeds from ammonia or its carbonate, a large number of substances (those which are insoluble in these reagents) must be absent. If it is due to the presence of the fixed alkalies or their carbonates, a still larger number of substances are excluded. If it is occasioned by the sulphides of the alkaline, or alkaline earth metals, all the metals whose sulphides are insoluble in water and alkaline sulphides must be absent. Examine for the basic constituents in the usual manner, paying strict attention to the precautions given in pars. 376 and 377. Commence the examination of the acids by rendering the solution exactly neutral with  $\text{HNO}_3$ . If no precipitate is produced on neutralizing the solution, proceed with the examination according to par. 550; if a precipitate is produced on neutralizing the solution, filter, examine the filtrate according to par. 550; and treat the precipitate according to par. 547.

647. The student should never employ the whole of the solution at his disposal, but should always reserve a portion, in the event of any unforeseen accident occurring, and for confirmatory experiments.

648. If the liquid under examination contains inorganic matter in suspension,\* the latter, after being separated by filtration, must be brought into solution according to the methods described under the head of "Solid Substances." The solid and liquid portions ought in most cases to be examined separately.

649. Answers to the following exercises must be written out.

\* The method of preparing for analysis a solution which is thick or turbid from the presence of organic matter, is described under the head of "Solid Substances containing Organic Matter" (par 731).

## EXERCISES.

170. A solid inorganic substance volatilizes completely at a heat below redness. How does this observation simplify its subsequent examination?

171. A solution is neutral to test-paper, and the only metals present are K, Na, and Ca, what acids must be absent?

172. A solution is alkaline to test-paper, the alkalinity is due to the presence of ammoniac carbonate; what substances must be absent?

173. A solution acid to test-paper is colorless, what substances must be absent?

174. A solution acid to test-paper contains Ba and Ag, what acids must be absent?

## EXAMINATION OF SOLIDS.

650. The substance is first examined as to its lustre, color, odor, and whether it is crystalline or amorphous, since these will frequently afford a means of classifying the substance. Thus, a metallic lustre will indicate probably a pure metal or any alloy. A blue color will indicate the probable presence of some salt of copper; a crystalline structure the probable presence of salt.

651. THE SUBSTANCE WILL EITHER BE A PURE METAL OR AN ALLOY, OR IT WILL NOT.

652. *If it is a pure metal or an alloy*, treat it according to par. 737, *after* it has been examined in a glass tube closed at one end and exposed on charcoal to the reducing flame of the blowpipe\* (see pars. 656, 2d and 4th).

653. *If it is neither a pure metal nor an alloy*, it will be free from or contain ORGANIC MATTER which will be ascertained in making the preliminary experiment (par. 656, 2d). *When it is destitute of organic matter*, treat it according to par. 717. *When it contains organic matter*, according to par. 731.

654. It has already been stated that the substance is submitted to different blowpipe operations before ascertaining in what liquid it will dissolve; the blowpipe operations and the order in which they are to be performed are described in the next paragraph. In these blowpipe experiments, only small quantities of the substance ought to be

\* These are the only blowpipe experiments which require to be made with a pure metal or an alloy.



employed; for if too much is operated upon, uncertain results are the consequence. A particle the size of a mustard seed is sufficient, and that of the flux added about the size of a hemp-seed. In reductions, a larger quantity may be employed, because, in that case, the more metal is produced, the more easily can its nature be ascertained. In all cases the substance operated upon must be reduced to the finest powder.

655. We give—Ist, *the blowpipe operations*; and 2d, *Bunsen's flame reactions*.\* We recommend the student to make himself acquainted with both modes of examination.

656. The following are the principal blowpipe operations and the order in which they are to be performed:—

1st. Examine whether the substance imparts a color to the flame, see Table page 238, and par. 660.

2d. Examine the substance in a glass tube closed at *one* end, see Table VIII. and par. 670.

3d. Examine the substance in a glass tube *open* at both ends, see par. 676.

4th. Expose the substance to the inner blowpipe flame on charcoal, see Table IX. and par. 682.

5th. Treat the substance with protonitrate of cobalt on charcoal, see Table X. and par. 684.

6th. Examine the substance with carbonate of soda on charcoal, see Table X. and par. 685.

7th. Fuse a portion of the substance with borax on platinum wire, see Table X. and par. 700.

8th. Examine the substance as to its fusibility, see par. 702.

657. COLORATION OF THE FLAME.—As many substances tinge the lamp flame with various characteristic colors, the substance under examination ought to be submitted to the flame in order to ascertain the presence or absence of these substances. To obtain the color the substance ought to be exposed to the flame on a platinum wire, and the experiment ought to be conducted in a dark room.

658. Merz, who has made a complete investigation of this subject, employs Bunsen's burner, and also a flame of pure hydrogen, and in addition makes use of *blue, violet, red, and green* glasses. The substances which he describes as giving characteristic colors to the flame of Bunsen's burner, in addition to those previously known, are nitric and chromic acids, while phosphoric and sulphuric acids give a

\* The student must study carefully the paragraphs under the head "Blowpipe," in Part III., when he makes these experiments.

peculiar coloration to the dark core of the flame of hydrogen.

659. The flame of Bunsen's burner gives three sorts of color: *a.* **BORDER COLORS.** These are of course peculiar only to the most volatile substances. To produce them, the loop of platinum wire is to be held outside of the flame about one or two millimetres from the lower portion of the outer limit. *b.* **MANTLE COLORS**—those, namely, which are seen when the substance is held in the bright blue-colored mantle which forms the outer portion of the flame. *c.* **FLAME COLORS.** To produce these, the loop is to be held horizontally and in the hottest part of the mantle. The hydrogen flame yields another species of color, viz., the **CORE COLORS.** These are produced only by sulphuric and phosphoric acids, which communicate respectively a blue and green tinge to the cold core of the hydrogen flame.

660. The following is a list of the substances\* which color the flame, with the color they impart:—

#### BLUE FLAMES.

(Consult pars. 661 and 662.)

Intense blue	.	.	.	.	Cupric chloride.
Pale clear blue	.	.	.	.	Lead
Light blue	.	.	.	.	Arsenic.
Greenish blue	.	.	.	.	Antimony.
Blue mixed with green	.	.	.	.	Cupric bromide.
Blue core color	.	.	.	.	Sulphuric acid.

#### GREEN FLAMES.

(Consult pars. 663, 664, and 665.)

Bronze-green border color	.	.	.	.	Nitric and Nitrous acids.
" " " "	.	.	.	.	Ammonic compounds.
" " " "	.	.	.	.	Cyanogen "
Greenish-blue border color	.	.	.	.	Hydrochloric acid.
Green mantle color	.	.	.	.	Boracic acid.
Gray yellow-green border color	.	.	.	.	Phosphoric acid.
Yellowish-green flame color	.	.	.	.	Baric compounds.
Dark green	.	.	.	.	Iron wire.
Full green	.	.	.	.	Copper.
Intense emerald green	.	.	.	.	Cuprous iodide.
Emerald green, mixed with blue	.	.	.	.	Cupric bromide.
Pale green	.	.	.	.	Phosphoric acid.
Intense whitish-green	.	.	.	.	Zinc.

\* In this list only the more commonly occurring substances are given.

## RED FLAMES.

(Consult pars. 666, 667, and 668.)

Intense crimson . . . .	Strontic compounds.
Reddish purple . . . .	Calcic compounds.
Violet . . . .	Potassic compounds.
Dark brownish-red border color } and a rose-red mantle color }	Chromic acid.

## YELLOW FLAMES.

(Consult par. 669.)

Yellow . . . .	Sodic compounds.
Feeble brownish-yellow . .	Water.

661. BLUE FLAMES.— $\text{CuCl}_2$  gives an azure-blue zone, and  $\text{Cu}(\text{NO}_3)_2$  a pure green flame color. By the combined observation of both colors, Cu may be distinguished from all other metals which give similar colors. The other flame coloring metals, such as As, Sb, Sn, Pb, Hg, and Zn exhibit, especially in the form of chlorides, more or less intense bluish or greenish mantle colors, which, however, cannot be advantageously used as reactions for the metals themselves.

662. Sulphuric acid produces a beautiful blue core color, being reduced to  $\text{SO}_2$ . The free acid gives the color when the platinum loop is held in the border of the flame, but a sulphate must be held in the middle of the flame. In the latter case, it is well to dip the test into strong HCl or fluosilicic acid.

663. GREEN FLAMES.—Nitric and nitrous acids give a bronze-green border color, usually with an orange-colored border. The test is to be previously dried in the flame, and dipped into a solution of  $\text{KHSO}_4$ , or into dilute HCl, according as we wish to test for nitric or nitrous acid. Ammonic and cyanogen compound give the same bronze-green border, but more faintly. HCl gives a very weak greenish-blue border color, which lasts for a very short time, and therefore does not deserve attention. The acid is however decomposed, and the Cl may easily be recognized.

664. Boracic acid gives a beautiful green mantle color, which is so intense that the acid may be recognized in the presence of large quantities of phosphoric acid. Borates are to be decomposed with  $\text{H}_2\text{SO}_4$ . Phosphoric acid gives

a gray yellow-green border color as well as a beautiful green core color. The dry test is to be dipped into  $\text{H}_2\text{SO}_4$  and held in the flame in the manner already pointed out, in order to show the border color. The green core color is less sensitive, but indispensable in recognizing phosphoric acid in the presence of large quantities of boracic acid, and is produced by alternately moistening the test with a solution of fluosilicic acid, and igniting it in the hydrogen flame, until the color distinctly appears.

665. Ba may be recognized by the yellowish-green flame color which appears blue green through the green glass. If the green disappears, and a red flame color makes its appearance, the test is to be repeatedly moistened with  $\text{HCl}$ , and immediately introduced while wet into the hottest part of the flame. When the blue-green color is no longer seen, proceed to examine for Ca.

666. RED FLAMES.—Ca is present when the red flame color, on evaporating the last portion of  $\text{HCl}$ , appears siskin green through the green glass. Sr gives in this case a weak yellow. Sr may be recognized by the purple or rose color which is seen through the blue glass, when the test, after moistening with  $\text{HCl}$ , is evaporated to dryness in the flame.

667. K gives a gray-blue mantle color, and a rose-violet flame color. These colors appear reddish-violet through the blue glass, violet through a violet glass, and blue-green through a green glass. The test is to be moistened with  $\text{H}_2\text{SO}_4$ , and repeatedly exposed to the flame for a short time.

668. Chromic acid gives a dark brownish-red border color, and a rose-red mantle color. The dry test is to be moistened with concentrated  $\text{H}_2\text{SO}_4$ , and held in the border. Chromic oxide gives no color, and is to be first oxidized to chromic acid by moistening with a solution of sodic hypochlorite and drying.

669. YELLOW FLAMES.—Na gives an orange-yellow flame color, which in very large quantities appears blue, but in small quantities is invisible through the blue glass. Through the green glass the flame appears orange-yellow, even with the smallest quantities; this glass is particularly adapted to the recognition of Na in all its compounds. The test is to be moistened with  $\text{H}_2\text{SO}_4$ , dried and held in the hottest point of the flame.\*

\* For this description of flame coloration I am indebted to Merz's paper on the subject.

670. EXAMINATION OF THE SUBSTANCE IN THE GLASS TUBE CLOSED AT ONE END.—The tube\* having been thoroughly cleaned and dried, a *small portion*, in the state of powder, of the substance to be examined is introduced into it, and heated over a spirit or gas lamp, at first gently in order to ascertain whether any VOLATILE SUBSTANCES OR ORGANIC MATTER form part of it; the tube is subsequently heated more strongly with the blowpipe until the glass begins to soften; for the changes consult Table X., and pars. 671, 675.

671. GASES OR FUMES ESCAPE.—“Observe whether they have a color, a smell, an acid or alkaline reaction, whether they are inflammable, etc.

1st. “*Oxygen*.—The disengagement of this gas indicates the presence of peroxides, chlorates, nitrates, etc. A glimmering slip of wood is relighted in the gaseous current.

2d. “*Sulphurous acid*.—This is often produced by the decomposition of sulphates, it may be known by its peculiar odor and by its acid reaction.

3d. “*Hyponitric acid*, resulting from the decomposition of nitrates, especially with oxides of the heavy metals; it may be known by the brownish-red color of the fumes.

4th. “*Carbonic acid*.—The evolution of  $\text{CO}_2$  indicates the presence of carbonates decomposable by heat. The gas evolved is colorless and tasteless, non-inflammable; a drop of lime-water on a watch-glass becomes turbid on exposure to the gaseous current.

5th. “*Carbonic oxide*.—The escape of this gas indicates the presence of oxalates and also of formates. The gas burns with a blue flame. In the case of oxalates the  $\text{CO}$  evolved is generally mixed with  $\text{CO}_2$ , and is therefore more difficult to kindle; in the case of formates the evolution of the gas is attended with marked carbonization. Oxalates evolve  $\text{CO}_2$  when brought into contact with  $\text{MnO}_2$ , a little water, and some concentrated  $\text{H}_2\text{SO}_4$ , on a watch-glass; formates evolve no  $\text{CO}_2$  under similar circumstances.

6th. “*Cyanogen*.—The evolution of  $\text{CN}$  denotes the presence of cyanides decomposable by heat. The gas may be known by its odor, and by the crimson flame with which it burns.

7th. “*Hydrosulphuric acid*.—The escape of  $\text{H}_2\text{S}$  indicates the presence of sulphides containing water; the gas may be readily known by its odor.

\* For the size of the tubes see “Blowpipe,” Part III.

TABLE VIII.

EXAMINATION OF THE SUBSTANCE IN A GLASS TUBE CLOSED AT ONE END.

(See par. 670.)

GASES OR FUMES ESCAPE. (See par. 671.)	
WATER CONDEENSES ON THE SIDES OF THE TUBE . . . .	Examine whether it has an <i>alkaline</i> or <i>acid</i> reaction; if the former probably due to $\text{NH}_3$ . (See par. 672.)
<i>A sublimate is formed. (See par. 673.)</i>	
Volatile Metals. (See par. 673 a.)	<div> <div> <div>ARSENIC . . . .</div> <div>ANTIMONY OXIDE . . . .</div> <div>ARSENIOUS ACID . . . .</div> <div>ARSENIC ACID . . . .</div> </div> <div> <div>The interior surface of the sublimate is crystalline.</div> <div>Fuses into a yellow liquid before subliming.</div> <div>Condenses in white crystals or powder.</div> <div>Converted into <math>\text{As}_2\text{O}_3</math> and <math>\text{O}</math>.</div> </div> </div>
	<div> <div>MERCURY . . . .</div> <div>ARSENIOUS ACID . . . .</div> </div> <div> <div>The odor of garlic is evolved.</div> <div>Condenses in liquid drops.</div> </div>
	<div> <div>CADMIUM . . . .</div> <div>ARSENIC ACID . . . .</div> </div> <div> <div>Gives a yellowish-red coating to charcoal when heated on it in the open air.</div> </div>
Volatile Metallic Oxides. (See par. 673 b.)	

TABLE VIII.—Continued.

<i>Volatile Salts.</i> (See par. 673 c.)	{ AMMONIC SALTS . . .	Volatilized unaltered except when the $\text{NH}_4$ is in combination with a fixed acid.
	{ MERCURIC CHLORIDE . . .	Melts before subliming.
	{ MERCURIUS CHLORIDE . . .	Sublimes without previous fusion.
	{ MERCURY IODIDE . . .	Forms a yellow sublimate.
	{ MERCURY SULPHIDE . . .	Forms a black sublimate.
<i>Non-metallic Bodies.</i> (See par. 678 d.)	{ PLUMBIC CHLORIDE . . .	Fuses before it sublimes.
	{ SULPHUR . . .	Forms a yellow sublimate.
	{ OXALIC ACID . . .	Forms a white crystalline sublimate.

*The substance does not volatilize, or not completely.*

- IT LIQUEFIES. (See par. 674 a.)  
 IT BLACKENS (carbonizes). (See par. 674 b.)  
 IT CHANGES COLOR. (See par. 674 c.)

8th. "*Ammonia* resulting from the decomposition of ammoniac salts, or also of cyanides or nitrogenous organic matters, in which latter case browning or carbonization of the substance takes place, and either cyanogen or offensive empyreumatic oils escape with the  $\text{NH}_3$ ."—Fresenius's "Chemical Analysis."

9th. *Nitric acid, fluorine, chlorine, bromine and iodine.*—The detection of these in the preliminary examination is best effected by mixing the substance under examination with rather more than its own weight of fused  $\text{KHSO}_4$ , and then heating the mixture in a glass tube closed at one end; before making the examination the student ought to consult pars. a, b, c.

a. *Nitric acid.*—If a nitrate is present, nitrous fumes are disengaged, the color of which may be best perceived by looking directly down the neck of the tube, inasmuch as a thicker stratum of the gas is in this way seen.

b. *Fluorine.*—According to Berzelius the substance ought, for the examination of F, to be mixed with four times its weight of fused  $\text{KHSO}_4$ , and the tube, after the introduction of the mixture, strongly heated with the blow-pipe flame until  $\text{H}_2\text{SO}_4$  begins to be evolved, and in order to avoid too great frothing up, the mass should be heated from the top downwards. If F is present, the tube will be encrusted more or less with silica deposited from the fluosilicic acid gas which passes off. The lower extremity of the tube containing the fused mass is then cut off, and the upper part rinsed out with water and dried with blotting-paper. If much F is present in the substance operated upon, the glass tube will be dull all over its inner surface, but if a small quantity only is present, the corrosion will be only partial.

c. *Iodine, bromine, and chlorine.*—Violent fumes of I are evolved, along with  $\text{SO}_2$ , on heating a substance containing an iodine compound with  $\text{KHSO}_4$  in the tube; some of the I is generally deposited as a black sublimate on the upper part of the tube. Br and Cl are in like manner evolved from their compounds.

672. AQUEOUS VAPORS ARE GIVEN OFF.—The water may have existed either mechanically, or as water of crystallization, or as constitutional water. If the body decrepitates on ignition, the decrepitation is due probably to the presence of an anhydrous salt which contains water mechanically between its crystalline plates, and the expulsion of which gives rise to the decrepitation. If the water is



present as water of crystallization, the crystalline body will generally fuse during the expulsion, and resolidify after it; some substances swell considerably during the expulsion—borax and alum for example. If the water comes from some decomposable hydrate, the substance will not fuse during its explosion.

673. A SUBLIMATE IS FORMED.—The sublimate may be due to some volatile metal, metallic oxide, volatile salt, or non-metallic body.

*a. The volatile metals* are principally As, Hg, and Cd; these metals form a black or gray sublimate having more or less of a metallic lustre. As is sublimed not only when it exists in its free state, but also from some metallic arsenides, which are decomposed by heat into As and an arsenide containing a less quantity of arsenic; a few arsenites also yield As, when heated out of contact with the air. Hg may be sublimed from most of its compounds; if the quantity is inconsiderable, it may only yield a gray sublimate; the globules can sometimes be rendered apparent by touching the sublimate with a glass rod, or on examining the sublimate with a lens. Cd may be sublimed from some of its alloys; it may be recognized by heating it in contact with the air, when it becomes converted into the brownish-yellow oxide.

*b. VOLATILE METALLIC OXIDES.*— $\text{Sb}_2\text{O}_3$  first fuses into a yellow liquid, and then sublimes under the form of shining crystalline needles. The sublimate  $\text{As}_2\text{O}_3$  may either be in the form of shining crystals or in the form of a white powder, which the magnifying-glass reveals, however, to be crystalline.

*c. VOLATILE SALTS.*—*Ammonic salts* form white sublimates; heated with NaHO and a drop of water on platinum foil, they evolve  $\text{NH}_3$ .  $\text{HgCl}_2$  begins to melt at a very gentle heat, and then sublimes;  $\text{HgCl}$  sublimes without previous fusion; the sublimate has a yellowish tinge whilst hot, but is perfectly white when cold.  $\text{HgI}_2$ , which is red, yields a yellow sublimate which becomes red by trituration.  $\text{HgS}$  gives a black sublimate which acquires a red tint when rubbed. When mercury compounds are mixed with NaHO, and then heated in the tube, a sublimate of mercurial globules will be obtained.  $\text{PbCl}_2$  first fuses and then sublimes. The sublimate of arsenic sulphide may be easily mistaken for pure sulphur.

*d. NON-METALLIC BODIES.*—S sublimes in reddish-brown drops, which solidify on cooling, and turn yellow or yel-

lowish-brown. The S may be present merely in the state of mixture, or it may be combined with some metal which abandons a portion of it when heated out of contact of the air. *Oxalic acid* yields a white crystalline sublimate, attended with thick fumes; the sublimate, when heated on platinum foil with a drop of concentrated  $\text{H}_2\text{SO}_4$ , gives rise to a copious evolution of gas.

674. THE NON-VOLATILE MATTER.—The non-volatile portion of the substance may liquefy, carbonize, or merely change color:—

a. If it liquefies without expulsion of aqueous vapor, and resolidifies when the heat is removed, the liquefaction may be due to various substances, as argentic chloride, the alkaline nitrates and chlorates, etc. If, by intense heat, O is evolved, and if a small piece of charcoal on being thrown into the fused mass is readily consumed, *nitrates* and *chlorates* are indicated.

b. If it carbonizes, organic matter is present. "Carbonization is always attended with evolution of gases (acetates evolve acetone) and water, which latter has an alkaline or acid reaction. If the residue effervesces with acids, whilst the original substance did not show this reaction, organic acids may be assumed to be present in combination with the alkalies or alkaline earths."

c. *It changes color.* "From white to yellow, turning white again on cooling, indicates  $\text{ZnO}$ ; from white to yellowish-brown, turning to a dirty light yellow on cooling, indicates  $\text{SnO}_2$ ; if the color changes from white to brownish-red, turning to yellow on cooling, and the body is fusible at a red heat, this indicates the presence of  $\text{PbO}$ ; if the color changes from white, or pale yellow, to orange-yellow, or to a deeper and more reddish tint up to reddish-brown, becoming pale yellow on cooling, and the body fuses at an intense heat, this indicates the presence of  $\text{Bi}_2\text{O}_3$ ; if the color changes from red to black, turning reddish-brown again on cooling, this indicates the presence of  $\text{Fe}_2\text{O}_3$ ; if the color changes from yellow to dark orange, and the body fuses at an intense heat, this indicates  $\text{K}_2\text{CrO}_4$ , etc."

675. In case of the non-appearance of any of these reactions, it must not be always concluded that the above-mentioned bodies are entirely absent; for S and As may be present in such forms that the simple application of heat will either not sublime them, or will expel them in combinations which afford none of the distinctive charac-

ters of the simple bodies; moreover, two or more of these may be present together in a substance, and afford sublimes having mixed characters, so that the individual elements are difficult to distinguish. Such is frequently the case with As and S, which, together, form a coating on the tube having a metallic lustre at its lower extremity, and passing upwards successively into black, brown, red, and finally yellow—these colors being due to combinations of S and As, which are more volatile than As; therefore, the examination of a substance in the glass tube affords frequently no positive indication of the presence of a body, but merely intimates its probable existence, to establish which further investigations are necessary. Such intimations are, however, of importance, as they serve as guides in after-processes.

676. EXAMINATION IN THE OPEN TUBE.—A small particle of the substance, in powder, is introduced into the tube at about half an inch from its extremity, and gradually heated, the tube being held in a slightly inclined position, so that a current of air may pass fully through it. By this means the substance is roasted, or oxidized, and various matters contained in it are volatilized and pass off up the tube.

677. The roasting must be performed slowly, with a gradually increasing temperature, and with a good current of air\* passing through the tube, otherwise unoxidized matter may be volatilized, and the mineral substance clotted and fused together. If a perfect roasting be required, the substance, after being heated for some minutes in the tube, is shaken out into an agate mortar, remixed, and roasted, and this process is repeated until fumes are no longer evolved. (Consult pars. 678 to 681.)

678. Almost all *metallic sulphides* disengage on roasting  $\text{SO}_2$ ; some sulphides yield besides a sublimate of S.  $\text{SO}_2$  may be recognized by its odor, or by its decolorizing moistened Brazil-wood paper,† a strip of which ought to be introduced in the interior of the raised end of the tube.

679. FLUORINE.—Very minute quantities of F can be detected by the following method: "Microcosmic salt,

\* By inclining the tube more or less, we have the means of regulating the current of air; very little passes through the tube when it is held in a horizontal position, but it becomes more and more active as the tube is held more and more vertically.

† Prepared by moistening slips of fine printing-paper with decoction of Brazil wood.

which has been previously fused upon charcoal or platinum, is finely powdered and mixed with some of the substance to be examined, also finely pulverized. A portion of the mixture is introduced into an open glass tube, and the blowpipe flame so directed upon it that a part of the flame passes up the tube. By this means HF is formed (if the substance be free from silica), which passes up the tube, and may be recognized both by its peculiar pungent smell and by the mode in which it corrodes the sides of the glass tube, rendering them dull and opaque wherever any moisture condenses. If Brazil-wood paper, moistened, be exposed to the action of the gases passing up the tube, it will be colored yellow, affording another indication of the presence of F. If the substance also contains silica, fluoride of silicon will be formed, which also colors yellow moist Brazil-wood paper, and is decomposed by water,\* silica being formed, which, as the water evaporates, is deposited on the sides of the tube, and is clearly perceptible either with or without the aid of a lens. If now the tube be washed out with water and dried, it will be generally found corroded by the F, which leaves a dull spot wherever it attacks the glass. As this experiment requires the application of a strong heat, so that the glass tube is frequently softened and bent, thus interfering materially with the success of the experiment, *Smithson* has recommended a piece of platinum foil to be bent into the form of a gutter, and inserted to about half its length into the glass tube; the mixture of the fused microcosmic salt and the substance under examination is laid upon the projecting part of the platinum, and the flame so directed upon it that the products of combustion pass up the tube. This arrangement has the advantage that the fused substance does not come in contact with the glass tube, and the inconveniences attending the fusing and softening of the glass are altogether avoided."

680. A sublimate may be formed in the second operation when none has been formed in the first, as  $\text{Bi}_2\text{O}_3$  will be formed when the  $\text{Bi}_2\text{S}_3$  or a bismuth alloy (scarcely any sublimate is produced on roasting Bi itself) is present in the substance under examination, and  $\text{PbSO}_4$  will be formed if  $\text{PbS}$  is present; in like manner,  $\text{As}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_3$  will be formed if an arsenide or an antimonide is present. If the

\* Water will be present, owing to the products of the combustion of the lamp passing up the tube.

fumes formed have an odor of garlic it shows the presence of As.

681. All the sublimates which are formed by oxidizing substances in the open tube are white, but the colored substances which are volatilized in the closed tube are still more easily volatilized in the open tube; for it need scarcely be observed that most of the reactions produced in the closed tube are also produced in the open one.

682. EXAMINATION ON CHARCOAL.—Most of the reactions described in pars. 670 to 679 are also produced on the charcoal; but only those reactions which are special to this operation are noticed in Table IX. and text.

683. In addition to the points which require to be attended to, as pointed out in the table, it should be particularly noticed whether the substance disengages a peculiar odor, as As and S might be detected by the odors they produce;\* and it should also be noticed whether the substance fuses; the oxides and acids which fuse are the oxides of Sb, Bi, Pb, and Cu. "Most metallic sulphides fuse when heated before the blowpipe upon charcoal, and this effect often takes place with sulphides of those metals whose oxides are infusible; but many of these sulphides become rapidly oxidized during the operation, and exhale an odor of  $\text{SO}_2$  in the same way as when heated in the open tube, and are thus converted into metallic oxides. Most metals fuse before the flame of the blowpipe; and all of them, except those called noble, are subsequently oxidized by the exterior flame." After this examination is complete, the substance must still be retained on the charcoal for the examination with  $\text{Co}(\text{NO}_3)_2$ .

684. TREATMENT WITH COBALTIC NITRATE.—No explanation beyond that given in Table X. is required.

685. EXAMINATION WITH SODIC CARBONATE ON CHARCOAL.—The substance (in powder) under examination is mixed with an equal quantity of  $\text{Na}_2\text{CO}_3$ , and the mixture is made into a paste with a drop of water. After it has been dried at a moderate heat, it is exposed on the charcoal to the reducing flame of the blowpipe, the oxidizing flame spreading over the charcoal. (See Table X., and pars. 686 to 699.) Should no reduced metal make its appearance, after exposure for two or three minutes to the flame, a little KCN may be added, and the experiment

\* It must be remembered that charcoal becomes, on exposure to the blowpipe flame, covered with a *bluish-white ash*.

TABLE IX.  
EXAMINATION ON CHARCOAL. (See par. 682.)

If deflagration ensue, the presence of a <i>chlorate</i> or <i>nitrate</i> is indicated.			
<i>Substances which volatilize or pass off in vapor.</i>	<i>Substances which are not volatilized.</i>		
MERCURY, ARSENIC, CADMIUM, ANTIMONY, ZINC, AMMONIA, SULPHUR, and LEAD partly.	SILVER, COPPER, BISMUTH, LEAD, TIN, GOLD, PLATINUM, COBALT, NICKEL, MANGANESE, IRON, ALUMINUM, CHROMIUM, BARIUM, STRONTIUM, CALCIUM, MAGNESIUM, SODIUM, POTASSIUM, SILICA, ETC.		
Color of the different Sublimates.	Substances which yield colored incrustations.	Substances which are infusible, but become luminous.	Substances which fuse, or run into the charcoal.
MERCURY, ZINC, AMMONIA . . . White.	LEAD, } Yellow. BISMUTH, }	ALUMINA, BARYTA, STRONTIA, LIME, and MAGNESIA, and their salts.	SALTS OF THE FIXED ALKALIES.
ANTIMONY, white, imparting a greenish-blue color to the flame.			
CADMIUM . . . . . Red brown.			

TABLE X.

## BLOWPIPE OPERATIONS.

Heat the substance on CHARCOAL, with the blowpipe flame; then moisten it with a solution of $\text{Co}(\text{NO}_3)_2$ ; again strongly heat it in the <i>outer flame</i> . (See par. 684.)	Mix the substance with $\text{Na}_2\text{CO}_3$ , and expose the mixed mass to the inner blowpipe flame, on CHARCOAL. (See pars. 685 to 699.)	Heat the substance before the blowpipe on PLATINUM WIRE, with a bead of BOAX. (See pars. 700 and 701.)
Substances which yield <i>colored masses</i> when thus treated.	Oxides and other Combinations of the Metals which can be reduced to the <i>metallic state</i> .	Substances which give <i>colored beads</i> .
	<i>Oxide of</i>	<i>In the outer flame.</i>
ZINCIC OXIDE . . . Green.	BISMUTH . . . Brittle.	COPPER . . . } Blue.
ALUMINA, }	ANTIMONY . . . Brittle; volatilizes in white fumes, yielding an incrustation.	COBALT . . . } Reddish.
SILICIC ACID, }	SILVER . . . Malleable; very white.	IRON . . . } Yellow.
PHOSPHATES, }	TIN . . . . Malleable.	MANGANESE . . . } Anethyst.
MAGNESIA . . . . Pink.	LEAD . . . . Malleable, very.	CHROMIUM . . . } Green.
	COPPER . . . { Well known colors of the metals.	
STANNIC OXIDE . . . A bluish-green color.	GOLD . . . . { These three are reduced, but yield no metallic beads; they are rendered magnetic, and can therefore be at once distinguished from the rest.	<i>In the inner flame.</i>
	NICKEL . . . }	COPPER . . . } Red.
	COBALT . . . }	COBALT . . . } Blue.
	IRON . . . }	NICKEL . . . } Gray.
		IRON . . . } Green.
		MANGANESE . . . } Colorless.
		CHROMIUM . . . } Green.

To discover the reduced metal remove the fused mass from the charcoal and grind it up in a small mortar with water; allow it to stand a minute, and then pour off the water and the suspended matter in it, and continue to repeat the process until the metal remains at the bottom of the mortar, perfectly free from charcoal, etc. If it is brittle, it will be in the state of very small spangles; if malleable, it will have adhered to the mortar or pestle, or a portion of it, whilst the rest may be in large spangles.

continued for two or three minutes longer. Many of the metallic arsenides and sulphides require to be carefully roasted, and thus deprived of their As and S and the metals themselves oxidized, before they can be reduced by  $\text{Na}_2\text{CO}_3$ ; in this case, the residue which remains from the open-tube experiment can be employed. It must be remembered, however, that Cd as well as S and As may have been expelled by the roasting.

686. The metals which can be reduced by this means, besides Au, Pt, and Ag, are Pb, Sb, Sn, Cu, Zn, Bi, Ni, Co, Fe, Cd, As, and Hg. "Au, Ag, Cu, and Sn compounds yield metallic beads, but no incrustations; Fe, Ni, Co, and Pt compounds give neither beads nor incrustations; Bi, Pb, and Cd compounds produce a yellow or brown deposit on the charcoal; Sb and Zn give a white incrustation;\* As may easily be recognized by its odor."

687. If a globule has been obtained, it is necessary to ascertain whether it is malleable or brittle: "for this purpose, it is allowed to cool perfectly, and carefully removed with a pair of tweezers. Having been placed upon a little anvil,† and struck with a small hammer—or, if these two blowpipe instruments are not at hand, upon the bottom of a strong mortar, and struck sharply with the pestle—if brittle, it of course falls to powder (as in the case of Sb); if semi-malleable, it flattens out, at the same time breaking into several pieces (as with Bi); and if fully malleable, flattens out without breaking (like Pb).‡

688. "*The globule obtained is malleable.*—Pb (makes a black streak upon paper); a yellow incrustation is formed upon the charcoal. Sn; a slight white incrustation. Cu (known by its color). Ag.

689. "*The globule is semi-malleable.*—Bi; a yellow incrustation.

690. "*The globule is brittle.*—Sb; abundant white incrustation.

\* The ash of the charcoal may sometimes be mistaken by beginners for a sublimate, but it may be distinguished from such by remaining unaltered before the inner flame.

† The anvil is a small block of hardened steel about two inches square and three-quarters of an inch thick, polished upon one or more of its faces. The hammer is made of hardened steel, one face must be square with sharp edges, for trying the malleability of substances, and the opposite end should be bevelled off like a chisel to detach small fragments of minerals etc.

‡ To prevent the fragments from dispersing from the striking they may be folded in a piece of thin paper, the corner of which may be held during the operation.



691. "If no metallic globule is obtained, but shining metallic spangles are observed after levigation; probably Sn, Sb, or Cu."

692. MAGNETISM.—To ascertain whether the reduced metal is magnetic, an ordinary steel magnet must be presented to it; if any of the metallic particles are magnetic they will adhere to it. The trial may be made with far more delicacy by bringing the metallic particles near a magnetic needle which is supported on a centre, on which it turns.

693. Only one mineral, magnetic oxide of iron, possesses magnetic *polarity* and *attraction*, all other minerals, which are attracted by the magnet, possess attraction only. The magnetic character serves to distinguish a few of the mineral species, which otherwise have very close resemblances; especially, magnetic iron ore from specular iron, and magnetic pyrites from common pyrites.

694. Many minerals become attractable by the magnet, only after undergoing the high heat of the blowpipe; this is the result of a partial decomposition.

695. CUPELLATION.—This is the process of separating gold and silver from other substances by heat, and obtaining them in a state of purity. The following is Berzelius' method:—

696. "A small quantity of bone-ashes (in powder) is to be taken on the point of a knife, moistened with the tongue, and kneaded in the palm of the left hand, with a very little soda, into a thick paste. A hole is then made in a piece of charcoal, and filled with the paste, and its surface smoothed by pressure with the agate pestle. It is then to be gently heated by the blowpipe till perfectly dry (the soda only assists the cohesion, and may be omitted). The assay,\* previously fused with *pure* lead, is placed in the middle of this little cupel, and the whole heated by the exterior flame. When the operation is finished, the precious metals are left on the surface of the cupel. This experiment is so delicate that grains of Ag, visible to the naked eye, and, indeed, such as may be collected by the forceps and extended under the hammer, may in this way be extracted from the lead met with in commerce.

697. "If the button obtained by cupellation does not possess the color of Au, but appears white, the quantity

\* It would be better to roast the substance under examination with  $\text{Na}_2\text{CO}_3$  on charcoal before assaying it with the pure lead.

of Au is less than that of Ag, in which case, the button should be placed in a porcelain capsule, a few drops of  $\text{HNO}_3$  poured on it, and the capsule heated over the lamp.

698. "If the button does not contain more than a fourth part of its weight in Au, it becomes completely black, and then decomposes, the Ag being dissolved, while the Au remains in black flakes. When the silver button contains more than a fourth of its weight of Au, it is blackened, but the Ag is not dissolved. It is neither blackened nor dissolved, if the proportion of Au to Ag is nearly equal; in this case the button must be melted with twice its bulk of pure Ag, on charcoal, and again heated with  $\text{HNO}_3$ , by which the mass becomes black, and dissolves; the pure Au being left behind."

699. If the substance fuses into a transparent glass with the  $\text{Na}_2\text{CO}_3$ , it shows the presence of silica, par. 458.

700. TREATMENT WITH BORAX.—To obtain a bead of borax, one end of the platinum wire is bent into a small hook. This is heated in the blowpipe flame, and then dipped into the borax; a small portion of the borax will adhere to it, and this being fused in the flame, and while hot dipped again into the powdered borax, a fresh quantity will adhere, which is fused as before, and this continued until a bead of the requisite size is obtained. A great many metallic oxides dissolve in borax, forming colored glasses. If any metallic arsenides or sulphides are present, it is necessary to roast the substance in the way previously described (676) before making the examination with borax; and it is frequently advantageous, before roasting the powdered substance, to mix it with a little powdered charcoal, so as to prevent the formation of sulphates and arseniates.

701. While the bead of borax is still hot, it is touched with a small quantity of the powder of the substance under examination, and that which adheres is fused into it. The operator must then observe—1st, whether the substance is soluble or insoluble in borax; and 2d, the color of the borax bead in (1) the oxidizing flame, and (2) in the reducing flame, both in the hot and in the cold state. In performing this experiment, care must be taken not to dissolve up, in the first instance, too large an amount of the oxide or other substance under examination. If a small quantity afford no distinct reaction, more may be easily added. If, however, the color of the bead is too intense to be clearly distinguished, the bead may be jerked off the

wire, and that which still adheres fused up with a fresh quantity of borax, by which a paler and more transparent glass will be obtained.

702. EXAMINATION IN THE PLATINUM FORCEPS.—“If the operator has convinced himself by a preliminary experiment that the substance under examination does not, when heated, attack platinum,\* a small splinter of it is to be taken between the platinum forceps, and subjected to the oxidizing flame; but if the substance is very fusible, a piece of platinum wire, hooked at one end, may be used instead of the forceps. If, however, the substance be one which exerts a chemical action on platinum, and would therefore injure the forceps or wire, charcoal must be employed as the support.

703. “In order to test the fusibility of a mineral, a small splinter, having a sharp edge or point, should be broken off and held in the forceps at a short distance beyond the point of the inner blue flame, so that the sharp edge is strongly heated. If a gas flame be employed, the mineral must be held somewhat further from the point of the blue flame than is necessary in the case of an oil-lamp, in order to prevent any reduction taking place, which would materially interfere with the results. If a powdered substance is to be tested, or one which decrepitates when heated, and which must therefore be previously pulverized, the following process may be resorted to: A small quantity of the powder is made into a paste with water, and spread upon a piece of charcoal; it is then dried, and strongly heated with an oxidizing flame, it will then (generally) cohere sufficiently to allow of its being taken up between the forceps and tested in the usual manner. Care must be taken that the substance, if a fusible one, and one which acts upon platinum, does not fuse upon the platinum points of the forceps.

704. “Of the metallic oxides, the following only are fusible in the oxidizing flame, viz., the oxides of Cu, Pb, Sb, and Bi. Metallic sulphides are, with few exceptions, readily fusible under the blowpipe flame; these exceptions are ZnS and MnS.”

705. “Of the simple silicates, *i. e.* silicates with a single base, those of the alkalies are most fusible. The silicates

\* Platinum cannot be employed when compounds of the easily reducible metals, as Ag and Pb, are present.

of Ca and Mg are with a few exceptions practically infusible. Aluminic silicates are infusible.

706. "Of the iron silicates those of ferrous and magnetic oxide are very fusible, but the ferric silicates are practically infusible. Consequently, under the blowpipe flame, the fusibility of an iron silicate much depends upon whether it be submitted to the oxidizing or the reducing flame; for the ferric silicates infusible in the former become fusible and magnetic in the latter. If, therefore, a substance be infusible, or only very slightly fusible in the oxidizing flame, it may afterwards be submitted to the extremity of the reducing flame, since many substances infusible in the former become fusible on undergoing a partial reduction.

707. "The fusibility of a compound silicate, *i. e.* a silicate containing two or more bases, depends upon that of the simple silicates of which it is composed, but is generally greater than the mean of these latter. Thus many calcic and magnesian silicates, and calcic and aluminic silicates, are more fusible than any of the simple silicates which enter into their composition.

708. "According to their relative fusibility, minerals may be classified as follows:—

- I. Readily fusible to a bead.
- II. With difficulty fusible to a bead.
- III. Readily fusible on the edges.
- IV. With difficulty fusible on the edges.
- V. Infusible.

709. "In testing the fusibility of a mineral substance, it should be noticed whether, if fusible, a clear or opaque bead is obtained; also, whether the substance changes color, becomes magnetic, or exhibits any phenomena of intumescence, ebullition, etc., all of which are useful characters in indicating the nature of the mineral."

710. "The degree of fusibility is a very important point to ascertain, when the examination in question refers to the native *combinations of silica* and certain other *minerals*, for this characteristic feature displayed by the blowpipe is often the only one by which we may distinguish those which consist of earths, and which contain no notable quantities of metallic oxides, properly so called. Amongst the minerals most frequently met with, the following are infusible:—

Quartz,	Spinel,
Corundum,	Pleonaste,
Tourmaline (both that which	Gahnite,
contains alumina and even	Olivine,
that which contains soda),	Cerite,
Zircon,	Cymophane,
Cyanite,	Gadolinite (which, being
Phenakite,	heated, becomes suddenly
Lencite,	luminous, as if it caught
Talc,	fire),
Pyrophyllite,	Vitreous tin,
Apatite,	Rutile,
Gehlerite,	Titanic iron,
Apophyllite,	Tantalite,
Staurotide,	Turquoise,
Refractory clays,	Titaniferous oxide of iron,
Aluminic hydrate,	Chrome iron,
Magnesian hydrate,	Native oxides of iron,
Aluminic sulphate,	Yttrotantalite,
Calcic carbonate,	Diopside,
Magnesian carbonate,	Chondrodite,
Zincic carbonate,	Topaz.
Allophane,	

711. "Amongst those which are almost infusible and only become rounded at the edges, the following may be named:—

Felspar,	Emerald,
Albite,	Titanite,
Petalite,	Sodalite,
Labradorite,	Calcareous Scheelin,
Anorthite,	Meerschauum,
Nepheline,	Soapstone,
Tubular spar,	Serpentine,
Pyroxène (which contains	Mica (some species, especially
much magnesia),	those found in granite),
Epidote (which intumesces	Dichroite,
by the first impression of	Heavy spar,
the heat),	Celestine,
Euclase (which intumesces by	Gypsum,
the first impression of the	Apatite,
heat),	Fluor spar.

*Table of Volatile Elements which*

	Metallic-film.	Oxide-film.	Oxide-film with stannous chloride.	Oxide-film with stannous chloride and soda.	Oxide-film with silver-nitrate and ammonia.
Te	Black ; thin part brown.	White.	Black.	Black.	Yellowish-white.
Se	Cherry-red ; thin part brick-red.	White.	Brick-red.	Black.	White.
Sb	Black ; thin part brown.	White.	White.	White.	Black ; insoluble in ammonia.
As	Black ; thin part brown.	White.	White.	White.	Lemon-yellow or reddish-brown ; soluble in ammonia.
Bi	Black ; thin part brown.	Yellowish-white.	White.	Black.	White.
Hg	Gray non-coherent thin film.				
Tl	Black ; thin part brown.	White.	White.	White.	White.
Pb	Black ; thin part brown.	Yellow-ochre color.	White.	White.	White.
Cd	Black ; thin part brown.	Blackish-brown ; thin part white.	White.	White.	White ; in the thin parts turns bluish-black.
Zn	Black ; thin part brown.	White.	White.	White.	White.
Sn	Black ; thin part brown.	Yellowish-white.	White.	White.	White.

*can be reduced as Films.*

Iodide-film.	Iodide-film with ammonia.	Sulphide-film.	Sulphide-film with ammo- nium-sul- phide.	
Brown ; disappears for a time on breathing.	Disappears altogether on blowing.	Black to blackish- brown.	Disappears for a time.	Elements whose reduction-films are scarcely dis- solved in dilute nitric acid.
Brown ; does not wholly disappear on breathing.	Does not dis- appear on blowing.	Yellow to orange.	Orange, and then disap- pears for a time.	
Orange-red to yel- low ; disappears on breathing.	Disappears altogether on blowing.	Orange.	Disappears for a time.	
Orange-yellow ; disappears for a time on breath- ing.	Disappears altogether on blowing.	Lemon- colored.	Does not dis- appear.	
Bluish brown ; thin parts pink ; disappear for a time on breathing.	Pink to orange ; chest- nut colored when blowing	Burnt-um- ber-color to coffee- colored.	Does not dis- appear.	Elements whose reduction-films are with diffi- culty dissolved in dilute nitric acid.
Carmine-colored and lemon-yel- low ; does not disappear on breathing.	Disappears for a time on blowing.	Black.	Does not dis- appear.	
Lemon-yellow ; does not disap- pear on breath- ing.	Does not dis- appear on blowing.	Black ; thin parts bluish- gray.	Does not dis- appear.	
Orange-yellow to lemon-color ; does not disap- pear on breath- ing.	Disappears for a time on blowing.	Brownish-red to black.	Does not dis- appear.	
White.	White.	Lemon- colored.	Does not dis- appear.	Elements whose reduction-films are instantly dissolved in di- lute nitric acid.
White.	White.	White.	Does not dis- appear.	
Yellowish-white.	Yellowish- white.	White.	Does not dis- appear.	

708. "The following are fusible:—

Zeolites (most of them intumesce),	Hydroboracite,
Spodumene (which intumesces),	Datholite,
Mejonite (which froths up before fusing),	Botryolite,
Elæolite,	Cryolite,
Amphibole (most of which boil up whilst in fusion),	Mica (several species, especially those which contain lithia),
Pyroxène (those which contain no excess of magnesia),	Tourmaline (those which contain potash),
Idocrase (intumescs in fusing),	Axinite (intumescs whilst fusing),
Garnet,	Amblygonite,
Cerine,	Lazulite,
Orthite (boils in fusing),	Hailyne,
Ferruginous Scheelin,	Nosin,
Boracite,	Eudialyte,
	Pyrosmalite."— <i>Rose's Manual of Analysis.</i>

712. *Bunsen's flame reactions.*—Almost all the reactions which can be performed by means of the blowpipe may be accomplished with far greater ease and precision in the flame of the non-luminous gas-lamp.\* This flame, moreover, possesses several peculiarities which render it available for reactions, by which the smallest traces of many substances occurring mixed together can be detected with certainty when the blowpipe, and even still more delicate methods fail. The method of examination of the various parts of the flame for these flame reactions is described in pars. 1167 to 1173, and the special behavior of the bodies themselves has been described under the head of their special properties; we shall, therefore, only here give a table (given by Bunsen in his paper on flame reactions) of the volatile elements which can be reduced as films. This table contains some of the rarer elements which are not given in the book.

713. *When the student has completed the preceding preliminary experiments, he will be able to arrange the substance under examination UNDER ONE OF THE THREE FOLLOWING DIVISIONS:—*

\* See description of Bunsen's lamp in Part III.



714. THE SOLID IS NEITHER A PURE METAL NOR AN ALLOY, AND IS DESTITUTE OF ORGANIC MATTER. See par. 717.

715. THE SOLID IS NEITHER A PURE METAL NOR AN ALLOY, BUT CONTAINS ORGANIC MATTER. See par. 731.

716. THE SOLID IS EITHER A PURE METAL OR AN ALLOY. See par. 737.

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717. THE SOLID IS NEITHER A PURE METAL NOR AN ALLOY, AND IS DESTITUTE OF ORGANIC MATTER.

718. Before a solid can be acted upon by reagents, it must be brought into a state of solution. For this purpose it is submitted to the action of different fluids, and the one in which it dissolves is termed its solvent. The solvents employed in qualitative analysis are water,  $\text{HCl}$ ,  $\text{HNO}_3$ , and aqua regia. Water, when it can be employed, is always to be preferred.

719. The student must particularly guard against adding too much of the solvent, especially if it be an acid. To avoid this, he must add it in small quantities at a time, and apply heat after each addition. The substance should, before being submitted to the action of solvents, be reduced to the state of a very fine powder, and fifteen or twenty grains employed for the analysis. The whole of the substance must, however, never be employed, but always a portion kept in case of any unforeseen accident, or for confirmatory experiments. In ascertaining in what liquid the substance is soluble, the student ought only to employ about three or four grains of the substance; after he has ascertained the solvent he can then dissolve up the fifteen or twenty grains for the analysis.

720. The powdered substance is boiled in ten times its amount of water. *It all dissolves.*—Examine it according to par. 640. *A portion remains undissolved.*—Filter a few drops of the liquid, and evaporate them to dryness on platinum foil. If a large residue remains on evaporation, the whole of the solution must be filtered, and examined according to par. 640. The insoluble residue, after being well washed with boiling water, must be examined according to 721. If no residue remains on evaporating the aqueous solution, or at all events a very slight one, pour the remain-

der of the water off, and treat the insoluble substance according to 721.

721. The substance which was partly or entirely insoluble in water, is boiled in dilute HCl, and if not soluble in dilute, then in concentrated HCl.\* *It all dissolves.*—Treat the fifteen or twenty grains in the same way and proceed with the examination for the bases in the usual way, and for the acids according to 547.† *A portion remains undissolved.*—Ascertain if anything has dissolved, by evaporating a portion of the fluid to dryness on platinum foil. Should this be the case, place the tube, with its contents, on one side, and proceed with the next experiment.

722. A fresh portion of the original substance is boiled in  $\text{HNO}_3$ . *The substance dissolves.*‡—Remove as much of the free acid as possible by evaporation; dilute the concentrated solution with water, and then proceed with the examination for the bases in the usual way, and for the acids according to 547. *It does not dissolve.*—Allow it to settle; pour off one-half the acid, add a like quantity of concentrated HCl, and again boil. If a portion still remains undissolved, return to the strong HCl mixture (721); filter, and analyze the filtrate in the usual way. The residue insoluble in acids, after being well washed, must be treated according to 723.

723. The usually occurring substances, which are insoluble in water and acids, are the **BARIC, STRONTIC, CALCIC, and PLUMBIC SULPHATES, ALUMINA, FERRIC OXIDE, and their phosphates, the ARGENTIC and PLUMBIC CHLORIDES, CALCIC FLUORIDE, SILICATES, SILICA, and SULPHUR.**

724. A small portion of the residue, insoluble in water and acids, is heated on a slip of platinum foil. If  $\text{SO}_2$  is evolved along with the volatilization of the whole of the substance, sulphur only can be present. When other substances are present, add to another small portion a drop of  $(\text{NH}_4)_2\text{S}$ . If the color remains white, Ag, Pb, and probably Fe, are absent.

\* If HCl causes any effervescence, the evolved gas must be examined for  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ , and HCN, as directed under these acids.

† If the substance is silicate decomposable by HCl, treat it according to par 455.

‡ If the substance dissolves with the separation of a light-yellow colored mass of sulphur, it points out the presence of a sulphide. When  $\text{HNO}_3$  is employed as the solvent, as much of the free acid as possible ought to be removed by evaporation, before passing  $\text{H}_2\text{S}$  through the solution, as they decompose each other, the decomposition being attended with the separation of a large amount of sulphur.

725. A small quantity of the dry residue, in the state of a very fine powder, is mixed with four times its weight of a mixture of equal parts  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$ . The mixed mass is placed in a platinum crucible,\* and heated over a gas lamp for about half an hour; or, what is still better, the platinum vessel is placed within a Hessian crucible containing a little  $\text{MgCO}_3$ , and exposed to a full red heat, for the same length of time, in a furnace. The magnesian carbonate is employed to prevent the platinum from coming in contact with the Hessian crucible.

726. On cooling, the fused mass is boiled with water, and filtered. The filtrate is to be examined for the *acids* and *alumina*, the residue for the *bases*.

727. *Examination of the filtrate.*—To one portion of the filtrate add  $\text{HCl}$  until the solution is distinctly acid; evaporate to dryness, and ignite until acid fumes are no longer evolved. To the dried mass add dilute  $\text{HCl}$  and boil; if a residue remains, silicic acid is present. To the filtrate from the silica add  $\text{NH}_4\text{HO}$  in excess, and then warm the solution; if a precipitate is formed, it must be due either to alumina or its phosphate. After having filtered and washed the precipitate, examine it for alumina and aluminic phosphate according to Table V. In the filtrate from the alumina precipitate, or in the solution which has failed to give a precipitate, test for phosphoric acid by adding  $\text{NH}_4\text{Cl}$ , and then  $\text{MgSO}_4$ . Acidulate another portion of the original filtrate with  $\text{HCl}$ , and examine for sulphuric acid by adding  $\text{BaCl}_2$ . Another portion must be acidulated with  $\text{HNO}_3$ , and tested for chlorine by  $\text{AgNO}_3$ . To detect fluorine, an examination must be made according to 462 or 463.

728. *Examination of the residue.*—After having removed all the substances soluble in water, by repeated washings, dissolve the residue, if  $\text{Pb}$  and  $\text{Ag}$  are absent, in  $\text{HCl}$ , and proceed with the analysis in the usual way. If the residue does not completely dissolve in the acid, and the two metals just named are absent, it shows that a portion of the substance has not been decomposed. When this is the case, filter off, and examine the filtrate.

729. When the fixed alkalies are to be looked for in the

\* The compounds of the easily reduced metals, such as  $\text{Ag}$ ,  $\text{Pb}$ , etc., must not be fused in platinum vessels, as they form alloys with that metal, which greatly injures or altogether destroys the platinum vessel: porcelain crucibles must therefore be employed in such cases.

insoluble residue, another portion, in fine powder, must be mixed with about four times its weight of  $\text{BaCO}_3$ , and fused in a platinum crucible, in the manner already described. On cooling, the fused mass is digested with dilute  $\text{HCl}$ , and filtered. The filtrate is evaporated to dryness, and ignited; the dry residue must be treated with water, and again filtered. The filtrate, after being freed from iron oxide, alumina, baryta, lime, and magnesia (if present) must be evaporated to dryness, to expel the ammoniac salts which have been employed in their precipitation; if a residue remains, it must be examined for  $\text{K}$  and  $\text{Na}$ .

730. Bloxam has proposed to fuse insoluble substances by mixing them with a deflagrating mixture. A great saving of time and labor is thus effected by causing the heat to be applied *inside* the mass to be fused. The following is the process: 5 grains of the substance are intimately mixed with 10 grains of dried  $\text{Na}_2\text{CO}_3$  and 70 grains of the deflagrating flux, composed of charcoal\* and nitre in the proportion of one part by weight of the former to six of the latter. The mixture is placed in a *thin* porcelain dish, or clean iron tray, and a lighted match applied to the centre of the heap. The deflagration is completed in two or three seconds, and a well-fused mass remains. This is easily detached from the cooled dish (in which a little unburnt charcoal may be left), and boiled with water, being occasionally stirred with a glass rod. Two or three minutes always suffice for the extraction of the soluble portion, which is then filtered off, and examined for acids and for such bases as are compatible in solution with the alkaline carbonates (par. 727). The residue left by water, after having been washed, is treated with acids, and examined in the usual way (par. 728). A little charcoal is generally left undissolved by acids, and with it any of the substances which may have escaped decomposition. If it be thought necessary, the dried residue may be ignited until the charcoal is consumed, and the incombustible portion examined.

731. THE SOLID SUBSTANCE UNDER EXAMINATION IS NEITHER A PURE METAL NOR AN ALLOY, BUT CONTAINS ORGANIC MATTER.

\* The charcoal should, of course, be chosen so as to yield a very small proportion of ash, and must be reduced to a fine powder; the charcoal from the powder-mills is most suitable for the purpose. The nitre must be chemically *pure*.

732. The presence of fixed organic matter\* interferes with the detection of many substances. Thus, in the presence of tartaric acid, which is a fixed organic acid, aluminic, chromic, iron, and many other metallic oxides, are not precipitated by the alkalis; alkaline citrates prevent the precipitation of acids by bases, with which the acids form insoluble salts under ordinary circumstances; a soluble baric salt will not produce a precipitate, even in a solution of a sulphate, if an alkaline citrate be present, unless the sulphate is present in the proportion of three or more equivalents for every one of the citrate. Soluble plumbic and strontic salts produce, likewise, no precipitate in solutions of sulphates in the presence of citrates, the citrates interfere with the precipitation of a large number of substances, Mn, for instance, is not precipitated from its solutions by ammoniac sulphide.† It is therefore necessary, after precipitating the fifth and sixth groups by HCl and  $H_2S$ , to destroy the fixed organic matter, when it is present, which will have been ascertained in the preliminary examination. For this purpose, the filtrate from the  $H_2S$  precipitate, or the solution which has failed to give a precipitate with this reagent, is evaporated to dryness and ignited‡ until all the organic matter has been destroyed, the residue must then be dissolved in water or acids as directed at par. 718 and then examined for the 4th, 3d, 2d, and 1st groups of basic substances in the usual way. The examination of the acids must be conducted as directed at par. 720, and following pars.

733. Sometimes we are obliged to have recourse to the following method for destroying the organic matter, especially in the case of liquids and solids which have to be examined for *poisons*. The solid or liquid is placed in a porcelain dish, and to it is added pure concentrated HCl, about equal in weight to the *dry* solid present, and then, if re-

\* Organic substances are termed *fixed* when they cannot be distilled or volatilized without decomposition. The organic matter ought to be tested for nitrogen; for this purpose it is mixed with caustic potash in powder or with soda-lime, and the mixture heated in a test-tube, when, if it contains nitrogen,  $NH_3$  will be evolved.

† Spiller on the Influence of Citric Acid on Chemical reactions. Quarterly Journal of the Chemical Society of London, vol. x.

‡ Many substances, especially aluminic and the iron oxides, after ignition dissolve with very great difficulty even in the concentrated mineral acids. The residue may therefore require protracted boiling in acids, although the original substance dissolved in water or dilute acid very readily.

quired, water to make the mass of a thin pasty consistence, the dish is placed on the water-bath, and small portions of pure potassic chlorate are added every five minutes or so, stirring constantly at the same time the contents of the dish; the addition of the potassic chlorate is continued until the mixture is perfectly fluid and of a light-yellow color; when this is attained we add 20 or 30 grains more of the  $\text{KClO}_3$ , and continue the heat until the liquid ceases to smell of chlorine; the mixture is then filtered through paper or linen, the residue thoroughly washed, and the wash-water concentrated over the water-bath, and then added to the filtrate; the filtrate is examined as directed in the next par. The residue must be examined for  $\text{AgCl}$ ,  $\text{PbSO}_4$ , and  $\text{SnO}_2$ , as directed at par. 723.

734. The filtered liquid is placed in a flask and kept at a temperature between  $60^\circ$  and  $70^\circ \text{C.}$ , and washed  $\text{H}_2\text{S}$  transmitted through it for about twelve hours, it is then allowed to cool, and during the cooling the transmission of the gas through it is continued; it is then covered over with paper and placed in a moderately warm place, and allowed to stand for twenty-four hours; if at the end of that time it has only a faint odor of  $\text{H}_2\text{S}$ , the gas is again passed through it to excess, and it is again allowed to stand until the odor of  $\text{H}_2\text{S}$  has again nearly disappeared; the precipitate is then collected upon a filter and washed until the washings are quite free from  $\text{Cl}$ ; the filtrate is examined for the members of the 4th and 3d groups.

735. The precipitate contains, besides any metals that may be present, organic matter and sulphur; if the analysis has been instituted, not for the examination of the poisonous metals, the precipitate can be examined in the usual manner; but if the examination is made to ascertain whether any of the poisonous metals are present, it may be conducted in the following manner: Digest the precipitate for some time in  $\text{NH}_4\text{HO}$ ; the  $\text{As}_2\text{S}_3$  dissolves, and the other sulphides remain undissolved; filter off and evaporate the filtrate along with the wash-water to dryness on the water-bath, the  $\text{As}_2\text{S}_3$  will remain; it is generally of a brown color, from the presence of organic matter which has been dissolved by the  $\text{NH}_4\text{HO}$ . Examine the precipitate according to the electrolytic method (273), or according to the method described in par. 260.

736. The precipitate insoluble  $\text{NH}_4\text{HO}$ , after it has been thoroughly washed, is digested in yellow  $(\text{NH}_4)_2\text{S}$ ; it is then filtered, and the filtrate, along with the wash-water, is

evaporated to dryness over a water-bath; the residue is examined for  $\text{Sb}_2\text{S}_3$  by the usual tests. Treat the sulphides insoluble in  $(\text{NH}_4)_2\text{S}$  according to par. 294.

737. THE SUBSTANCE UNDER EXAMINATION IS A PURE METAL OR AN ALLOY.

738. Nitric acid behaves with metals in the following manner: Au and Pt are neither dissolved nor altered in the least degree by it. Sn and Sb are converted by it into oxides, which do not dissolve in or combine with an excess of the acid. The other metals are oxidized and converted by it into soluble nitrates. On account of the different behavior, therefore, which  $\text{HNO}_3$  exhibits with the metals, it is usual to employ it as the solvent of alloys, etc.

739. To the metal or alloy under examination, which is placed in a small flask, is added  $\text{HNO}_3$  of sp. gr. 1.20, and heat applied. One of the three following cases will then occur: 1. Complete solution takes place. 2. A white insoluble substance separates. 3. A metallic residue remains. Each of the three cases is considered separately in detail.

740. 1. *If complete solution ensues*, Au, Pt,\* Sn, and Sb† must be absent. After removing the greater part of the free acid by evaporation, dilute the solution with water,‡ and proceed with the analysis in the regular way. Hg, if present, will be found in the mercuric state.

741. 2. *If a white insoluble substance separates*, Sn or Sb is indicated. After removing the greater part of the free acid by evaporation, dilute the solution with water, filter, and proceed with the filtrate in the ordinary way. The precipitate, after being well washed with water, is treated with a hot concentrated solution of tartaric acid. If it all dissolves, Sn is absent. The presence of Sb is confirmed by  $\text{H}_2\text{S}$  producing in the tartaric acid solution, to which  $\text{HCl}$  has been added, an orange-red precipitate. If the whole of the *insoluble substance* does not dissolve in tartaric acid, the solution is filtered. The filtrate is examined for Sb by the method just stated. The residue, after being well washed, is mixed with  $\text{Na}_2\text{CO}_3$  and  $\text{KCN}$ , and exposed on a charcoal

\* Alloys of Ag and Pt, with the latter metal present in small proportion only, dissolve in  $\text{HNO}_3$ .

† Very minute traces of Sb are often completely dissolved by  $\text{HNO}_3$ .

‡ If the solution becomes turbid on the addition of water, it indicates the presence of Bi.

support to the inner blowpipe flame. If Sn is present, ductile metallic grains will be obtained.

742. 3. *If a metallic residue remains*, Au or Pt is indicated. After removing the greater part of the free acid by evaporation, dilute the solution with water, filter, and examine the filtrate in the usual way. The metallic residue is dissolved in aqua regia. One portion of the solution is tested for Au according to 284. The other portion is tested for Pt according to 287.

743. Answers to the following exercises must be written out.

#### EXERCISES.

175. If you had such a mixture as the following, whether would it be more advantageous to treat it, first with water until all the soluble matter was removed, and then with HCl, or to treat it at once with HCl: what difference would there be between the two modes of treatment:  $\text{Na}_2\text{SO}_4$ ,  $\text{KNO}_3$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{BaCO}_3$ ?

176. Whether would it be better to treat such a mixture as the following, first with water, and second with HCl, or to treat it at once with HCl:  $\text{Fe}_2\text{O}_3$ ,  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{MnCl}_2$ ,  $\text{As}_2\text{O}_3$ ,  $\text{CuSO}_4$ ?

177. Name the more frequently occurring mineral compounds which are insoluble both in water and acids, and describe the processes for rendering them soluble.

178. How would you perform the qualitative analysis of an alloy containing arsenic, copper, silver, lead, and iron?

179. Name the chief blowpipe reactions employed in qualitative analysis.



## PART II.

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### ANALYSIS OF ORGANIC SUBSTANCES.

744. ALL organic substances contain CARBON; a large number are composed of CARBON and HYDROGEN only; a still larger number contain OXYGEN in addition to the two last-named elements; and a large number are composed of CARBON, HYDROGEN, OXYGEN, and NITROGEN. A smaller number contain SULPHUR in addition to these four elements, and a still smaller number contain PHOSPHORUS. Organic substances, therefore, unlike inorganic ones, are all composed of some two, three, four, or five elements, and these elements are the same for all the different organic bodies. But although the formation of organic substances is restricted to some three, four, or five of the elementary bodies, their atomic constitution is far more complex than that of mineral substances, and this is one of the most marked distinctions between organic and inorganic bodies. For example, "a particle of common salt, or of cinnabar, presents a group of not more than two atoms, whilst an atom of sugar contains thirty-six elementary atoms, and the smallest particle of olive oil consists of several hundred simple atoms.

745. "It is upon the greater complexity of composition of organic bodies, together with the lesser force with which, consequently, their constituent atoms attract each other, that their easier decomposability depends: heat, for example, disturbs their composition with much greater facility than it does that of inorganic bodies. The atoms of the former, once put in motion, or by the action of heat being separated to a greater distance from each other, arrange themselves into less complex atoms, in which the force of attraction acts in fewer directions and in which it is consequently able to oppose a proportionably stronger resistance to the further action of causes of disturbance—decomposition."—*Liebig*.

746. Organic compounds may be analyzed either with a view simply to resolve them into their *proximate constituents*, as, for instance, resolving wheat flour into its proximate constituents, starch, sugar, gluten, ligneous fibre, and oily matter; this kind of analysis is called the *proximate analysis* of organic substances; or the analysis may have for its object the mere testing the organic compound for some one or two elements, as nitrogen and sulphur; this is called *elementary or ultimate analysis*.

747. We will first describe the method of testing organic substances for nitrogen, sulphur, phosphorus, and inorganic substances,\* and afterwards describe the proximate analysis of organic substances.

#### ELEMENTARY ANALYSIS.

748. *Test for an organic compound.*—As all organic substances contain carbon, and as very few of them contain oxygen in sufficient quantity to combine with the whole of their carbon and hydrogen, it follows that if they are heated in a closed vessel, as a small glass tube, so as to exclude the air, a black or carbonized residue will remain. No inorganic compound leaves a residue of carbon when heated under similar circumstances. Volatile bodies require to be mixed with  $\text{CuO}$  or  $\text{PbCrO}_4$ , and burned in a glass tube for the detection of their carbon, which is converted into  $\text{CO}_2$ , and if passed into a solution of  $\text{BaH}_2\text{O}_2$ , causes a white precipitate of  $\text{BaCO}_3$ , the H in the organic substance becomes converted into  $\text{H}_2\text{O}$ , which may be collected in drops in a cooled receiver, or passed through a tube containing  $\text{CuSO}_4$ , which has been dried at  $205^\circ \text{C}$ ., water changes the color of the dry cupric salt from white to blue.

749. *Tests for Nitrogen.*—Substances containing a tolerably large quantity of N, emit in burning the familiar smell of singed hair or feathers; if this smell is distinctly perceptible, no further test is required to confirm the presence of this element. When there is no distinct smell of burnt feathers, one of the two following tests may be employed:—

1st. The substance to be examined, which must be in the

\* Animal and vegetable substances are frequently composed of inorganic as well as organic compounds, and it is as necessary to determine the nature of the inorganic as of the organic matter.

solid state, is mixed with solid KHO or with *soda-lime*,\* the mixture is introduced into a dry test-tube, and then ignited; the C is converted into CO<sub>2</sub> by the O in the alkaline hydrate, while all or the greater part of the H combines with N when present, and forms NH<sub>3</sub>, which is evolved, and may be detected in the usual way (Table 1. A 2, page 34).

2d. "Lassaigne has proposed another method which is based upon the property of potassium to form KCN when ignited with a nitrogenous organic substance. The following is the best method of performing the experiment: Heat the substance under examination, in a test-tube, with a small lump of K, and after its complete combustion, treat the residue with a little water (cautiously); filter the solution, add two drops of solution of FeSO<sub>4</sub> containing some ferric salt, digest the mixture a short time, and add HCl in excess. The formation of a blue or bluish-green precipitate or coloration proves the presence of nitrogen (499).

"Both methods, 1st and 2d, are delicate; the 1st is the one most generally employed; it fully answers the purpose in nearly all cases.

3d. "If, however, the nitrogen exists in the organic compound in an oxidized state, it cannot be detected by either of the methods just given, but it may readily be detected by heating the substance in a tube, when the evolution of red acid fumes, imparting a blue tint to iodide of starch paper, will incontestably prove it."

750. *Tests for sulphur*.—If the substance is in the solid state, it may be mixed with about twelve times its weight of pure solid KHO, and about six times its weight of pure KNO<sub>3</sub>; or it may be intimately mixed with some pure KNO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>; the mixture is then heated to fusion in a crucible. The fused mass is allowed to cool, then dissolved in water, the solution acidified with HCl and tested subsequently for H<sub>2</sub>SO<sub>4</sub> with BaCl<sub>2</sub>.

751. Fluids are treated with fuming HNO<sub>3</sub>, or with a mixture of HCl and KClO<sub>3</sub>, at first in the cold, finally with heat; the solution is then tested for H<sub>2</sub>SO<sub>4</sub> with BaCl<sub>2</sub> or Ba(NO<sub>3</sub>)<sub>2</sub>.

752. As the two methods just described serve simply to indicate the presence of sulphur in a general way, but afford no information regarding the state or form in which that

\* Soda-lime is a mixture of CaO with NaHO. The lime is simply employed to prevent the soda fusing.

element may be present, we give another method (753), which serves to detect only the sulphur in the non-oxidized state in organic compounds.

753. Boil the substance with a strong solution of KHO, and evaporate nearly to dryness. Dissolve the residue in a little water, pour the solution into a flask,\* and slowly add dilute  $\text{H}_2\text{SO}_4$  through the funnel-tube, if sulphur is present the *lead test-paper* will turn brown.

754. *Tests for phosphorus*.—The methods described in pars. 750 and 751, will likewise serve for P. The solutions obtained are tested for phosphoric acid either according to par. 424, 427, or 428. If the method described in par. 751 has been employed, the greater part of the  $\text{HNO}_3$  must be removed before employing the test. The P may be detected by slightly carbonizing the substance, then reducing it to powder, and conducting the operation as at par. 431.

755. *Test for inorganic substances*.—"A portion of the substance under examination is heated on platinum foil, to see whether or not a residue remains. When acting upon difficultly combustible substances, the process may be accelerated by heating the spot which the substance under examination occupies on the platinum foil, to the most intense redness, directing the flame of the blowpipe upon the corresponding point of the lower surface of the foil." The methods for examining the residue are described in pars. 760 to 771.

#### PROXIMATE ANALYSIS OF ORGANIC SUBSTANCES.

756. Organic substances, like inorganic ones, are either acids, bases, salts, or indifferent bodies, and the resolution of organic compounds into their proximate constituents, is effected by methods perfectly similar to those used in the analysis of inorganic compounds; that is, the operator endeavors to separate (by solvents, application of heat, etc. etc.) the individual constituents from one another, either in the *direct* way, or after having previously converted them into appropriate forms.

757. Of the solvents employed in organic analysis ether is particularly valuable as a solvent for fatty substances, and for caoutchouc and camphor; alcohol, for the solution

\* The flask must be provided with a funnel-tube which is fitted into a cork, on the under surface of the cork is attached a slip of paper which has been thoroughly moistened with a solution of lead acetate, and then touched with a few drops of a solution of  $(\text{NH}_4)_2\text{CO}_3$ .

of many crystallizable organic principles, such as the vegetable alkalies; whilst water dissolves sugar, gum, starch, and other bodies, which are nearly insoluble in alcohol and ether. In some cases benzole, in others chloroform, is a valuable solvent, and may be substituted for ether, which they most resemble in their solvent action. In particular cases dilute acids, and in others dilute alkalies may be employed, but they must be used with caution, as they are liable to act not merely as solvents, but also to produce important chemical changes upon the compounds submitted to them. No general rule can be laid down for the extraction of the different proximate principles, each class of substances requiring special modifications, which experience alone can indicate.

758. In all cases of proximate analysis, the employment of the microscope will be found invaluable as a means of watching the progress of the separation of the various principles, and of ascertaining whether the substances which the chemist has isolated are mixed with other bodies which may resemble them in chemical habitudes. When a substance or deposit assumes the crystalline state, such an examination, by revealing the similarity or difference in form of its component particles, is often more valuable for ascertaining the purity of a substance than ordinary chemical reagents.—*Miller*.

759. We shall now give the method for the examination of the ash, whether derived from animal or vegetable substances, and we shall then give under Animal and Vegetable Chemistry the properties and reactions of the chief organic compounds of animal and vegetable origin, and along with this the proximate analysis of mixed animal substances and the analysis of urine.

#### EXAMINATION OF THE INORGANIC CONSTITUENTS OF ANIMAL AND VEGETABLE SUBSTANCES.

760. *Preparation of the ash*.—The incineration of the substance\* is best effected by placing it in a platinum dish, or other shallow vessel, and introducing the vessel into a muffle, which should then be gradually heated; but not carried beyond a very faint redness.† For merely qualitative

\* Before incinerating the substance care must be taken to free it from all adhering impurities, as these are frequently attached to plants.

† Substances to which this mode of incineration is unsuited, are charred first at a gentle red heat in a large covered platinum or Hessian crucible, and the charred mass is subsequently incinerated in the muffle

analysis it will generally be found sufficient to char the substance in a porcelain or platinum dish, with the aid of a wide glass tube or lamp-glass to increase the draught. "The heat must always be moderate to guard against the volatilization of certain constituents, more especially of metallic chlorides. It is not always necessary to continue the combustion until all the carbon is consumed. With ashes containing a large proportion of fusible salts, as *e. g.* the ash of beetroot molasses, it is even advisable at first, simply to char the mass in a crucible at the lowest possible temperature, then to treat with water until the principal portion of the soluble salts is extracted, afterwards dry the residue, and finally, incinerate it in the muffle" (*Fresenius*). Alkaline sulphates are frequently converted by the reducing action of carbon, into sulphides and hyposulphites. The ashes of animal substances often contain cyanates, which are best destroyed by moistening the ashes with water, and then gradually heating to redness; one moistening is usually sufficient to convert them completely into carbonates.

761. *Analysis of the ash.*—In the qualitative examination it is usual to examine the aqueous solution, the HCl solution, and the portion insoluble in acids separately—supposing the ash is not entirely soluble in water—as we thereby obtain a better acquaintance with its general character, and in the state or condition in which the constituents are present. In this examination we shall confine ourselves to the natural constituents of the ashes of plants and animals; if accidental constituents require to be sought for, a complete qualitative inorganic analysis, according to the methods given in Part I. of this work, must be undertaken.

762. The following are the natural constituents:—

<i>Bases.</i>	<i>Acids.</i>
Iron oxide.	Silica.
Manganese oxide.	Phosphoric acid.
Lime.	Sulphuric acid.
Magnesia.	Carbonic acid.
Soda.	Chlorine.
Potash.	Fluorine.
Lithia.*	Iodine.†

\* Lithia has lately been found in the ash of many plants; Rubidium has also been found, but this can only be discovered by spectrum analysis.

† Iodine and bromine need only be looked for in marine plants.

763. Boil the ash with water, filter, and examine the filtrate according to next par., and the portion insoluble in water after it has been well washed according to par. 767.

764. *Examination of the aqueous solution.*—Add to about one-half the aqueous solution  $\text{HCl}$ , if effervescence ensues, it may be due to  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ , or  $\text{SO}_2$ , arising from the decomposition of hyposulphites; examine the evolved gas for carbonic acid according to par. 441; the other two gaseous acids need not be attended to, as they, if present, are only due to the reduction of the alkaline sulphates (406).

765. Evaporate the solution, which has been acidulated with  $\text{HCl}$ , to dryness, treat the residue with  $\text{HCl}$  and water; if a portion remains undissolved it is due to silicic acid, in this case filter and add to the filtrate, or to the solution if there is no silicic acid,  $\text{NH}_4\text{HO}$  slightly in excess, and then acetic acid in excess, and then a drop of  $\text{Fe}_2\text{Cl}_6$  (427); if a precipitate is produced, phosphoric acid is present, in that case add more  $\text{Fe}_2\text{Cl}_6$  until the solution is of a slightly reddish color. Boil the solution whether phosphoric acid is present or not, in order to get rid of the iron which has been added; when all the iron has been precipitated, which is known by the complete decoloration of the liquid, filter, and to the filtrate add  $\text{NH}_4\text{HO}$  and  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ , if, after allowing the liquid to stand for some three or four hours, a precipitate is formed,  $\text{Ca}$  is present;\* filter and divide the filtrate into two parts, to one part add  $\text{NH}_4\text{HO}$  and  $\text{Na}_2\text{HPO}_4$ , if a precipitate is formed after some time,  $\text{Mg}$  is present. Evaporate the other portion of the filtrate to dryness, and ignite to get rid of and burn off all carbonaceous matter; examine the residue for  $\text{Na}$  (51), for  $\text{K}$  (46), and for lithia (61).

766. Add to a portion of the aqueous solution, which has not been acidified,  $\text{AgNO}_3$  as long as a precipitate continues to form; warm gently, and then cautiously add  $\text{NH}_4\text{HO}$ ; if a black residue is left, this consists of  $\text{Ag}_2\text{S}$ , proceeding from a sulphide or a hyposulphite. Mix the ammoniac solution—after previous filtration if necessary—cautiously with pure  $\text{HNO}_3$  in slight excess, to effect the solution of the precipitate of silver phosphate formed, thus leaving only  $\text{AgCl}$ ,  $\text{AgI}$ ,  $\text{AgBr}$  undissolved. Test sepa-

\* If  $\text{CO}_2$  is present,  $\text{Ca}$  and  $\text{Mg}$  must of course be absent, when this is the case, divide the filtrate from the silicic acid precipitate into two portions, test one for phosphoric acid by adding  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{HO}$ ,  $\text{MgSO}_4$  (424), and test in the other portion for  $\text{Na}$ ,  $\text{K}$ , and  $\text{Li}$ , in the manner directed in pars. 51, 46, 61.

rately for I according to 540, for Br 541, for Cl 539. Neutralize the filtrate from the portion of the Ag precipitate insoluble in  $\text{HNO}_3$  exactly with  $\text{NH}_4\text{HO}$ ; if on the neutralization, a *bright yellow* precipitate is produced, it is ortho-phosphoric acid that is present, but if the precipitate is *white*, the acid is either the pyrophosphate or the metaphosphate.\*

767. Warm then the portion of the ash insoluble in water, with  $\text{HCl}$ , if effervescence ensues it indicates  $\text{CO}_2$  combined with Ca or Mg; if Cl is evolved it denotes one of the higher manganese oxides.

768. *Examination of the hydrochloric solution.*—Add  $\text{NH}_4\text{HO}$  very slightly in excess, then add acetic acid in excess; if a white precipitate remains undissolved by the

\* If a phosphate contains three atoms of fixed base, the fluid, after the complete precipitation of the phosphoric acid by means of  $\text{AgNO}_3$ , will be neutral, but if it contained only two atoms or one atom of fixed base, the fluid after the precipitation of the acid with the silver salt, will be acid. Further, argentic ortho-phosphate ( $\text{Ag}_3\text{PO}_3$ ) is yellow, whilst argentic pyro-phosphate ( $\text{Ag}_4\text{P}_2\text{O}_7$ ), and meta-phosphate ( $\text{AgPO}_3$ ), are white. Again, an ortho-phosphate containing two atoms of fixed base is converted by ignition into a pyro-phosphate; and an ortho-phosphate containing one atom of fixed base is converted by ignition into a metaphosphate. We will now see how Liebig employed these facts in his investigation into the constitution of the ash of the juice of the flesh from different animals:—

Liebig found that the ash of the juice of the flesh in the case of the ox, horse, fox, and roe-deer, gave with water a strongly alkaline solution, and that it was precipitated, first white, then yellow, by neutral  $\text{AgNO}_3$ ; and the mixture, after complete precipitation, was perfectly neutral. This proves that the ash contains an alkaline pyro-phosphate and an alkaline ortho-phosphate. When this ash was mixed with  $\text{HNO}_3$ , dried up, and again ignited (by which means the Cl of the alkaline chlorides was expelled), and the metals added to the phosphates in the form of oxides, the proportion between the *white* and the *yellow* precipitate with  $\text{AgNO}_3$  was altered, the quantity of the yellow precipitate being increased; but the two colors of the precipitate were constantly observed.

The ash of the juice of the flesh of fowl, Liebig discovered, gave a different result. The aqueous solution gave with  $\text{AgNO}_3$  a precipitate of *pure white*; the ash, therefore, contains an alkaline pyro-phosphate, and when it was acted on by  $\text{HNO}_3$  and again ignited, the soluble portion still precipitated  $\text{AgNO}_3$  *only white*, although an additional quantity of alkali was thus added to the phosphate originally present. From this it follows, that the juice of the flesh of fowl must contain a certain, though small quantity of an alkaline meta-phosphate, since, otherwise, after the action of  $\text{HNO}_3$  on the ash, a certain quantity of an alkaline ortho-phosphate must have been produced, and thereby a yellow precipitate must have been formed, to a corresponding extent, with  $\text{AgNO}_3$ .



acetic acid it is due to the presence of ferric phosphate; filter a small portion of the liquid, and test for  $\text{Fe}'''$  with  $\text{K}_4\text{FeCy}_6$ , if it is present in the filtrate it shows that all the iron does not exist as phosphate; if there is no iron present in the filtrate add some  $\text{Fe}_2\text{Cl}_6$  to the unfiltered portion until the fluid looks reddish; in either case, that is, whether the iron is in excess or it is added in excess, boil the unfiltered portion until it is all removed; when this is accomplished filter hot, and add to the filtrate  $\text{NH}_4\text{HO}$  and  $(\text{NH}_4)_2\text{S}$ , and allow it to stand in a corked flask for some time; if a precipitate should form, test it for  $\text{Mn}$ ; filter and examine the filtrate for  $\text{Ca}$  and  $\text{Mg}$  in the usual way.

769. *Examination of the residue insoluble in hydrochloric acid.*—The residue insoluble in  $\text{HCl}$  contains—

1. The silicic acid which has separated on treating with  $\text{HCl}$ .

2. Those ingredients of the ash which are insoluble in  $\text{HCl}$ . These are, in most cases, ashes, sand, clay, carbon; substances, therefore, which are present in consequence of defective cleaning or imperfect combustion of the plants, or matter derived from the crucible. Only the ashes of the stalk of cereals and others abounding in silicic acid are not completely decomposed by  $\text{HCl}$ .

770. It is rarely necessary in an examination which is not going to be extended beyond a qualitative analysis to examine this residue further; but in cases where it is desirable, the analysis for all the bases, with the exception of the alkalies, must be conducted according to par. 725, and for the alkalies according to par. 729.

## ANIMAL CHEMISTRY.

771. We shall first give in groups, as far as it is possible, the chief organic compounds met with in the animal organism, with their properties and reactions; and afterwards a method for the proximate analysis of mixed animal substances (940), and lastly a method for the analysis of urine (964). Before commencing the proximate analysis the student is recommended to go through the chief groups, performing all the experiments given.

## THE ALBUMINOID OR PROTEIC GROUP.

ALBUMEN, FIBRIN, CASEIN, GLOBULIN, VITELLIN.

772. *Properties of the group.*\*—The members composing this group are met with in the vegetable as well as the animal kingdom; they are uncrystallizable, and in their pure state they are tasteless and inodorous. They exist in the living organism both in the soluble and insoluble state; they are present in the soluble form in the fluids, and in the insoluble form in the solid parts of plants and animals. When freshly precipitated from their solutions, and whilst still moist, they are usually whitish in color, and appear as a flocculent precipitate or in small clots; when dried and unpowdered they are tough and gelatinous.

773. These substances when dried, and if not exposed to moist air, will keep for any length of time unchanged. But if moist, or exposed to moisture, they speedily decompose and putrefy, and this is one of their most striking characters; they are *ferments* in their decomposing or putrefying state; yeast, wine-lees, diastase, synaptase, pepsin, for instance, are albuminoids in a peculiar state of decomposition.

774. If these bodies are heated in close vessels (subjected to dry distillation), they first swell up and fuse, then blacken, and emit a large quantity of fetid empyreumatic products, among which  $\text{NH}_3$  and  $\text{H}_2\text{S}$  are always present; and they leave in the retort a porous, brilliant, carbonaceous mass. When burned they leave a notable amount of ash; this varies in quantity in different cases, but it always contains phosphate of lime.

775. They all yield the same products when treated with oxidizing agents, such as  $\text{MnO}_2$ , or  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{H}_2\text{SO}_4$ ; the volatile products are the only class which have been fully examined; the following are the volatile substances which have been identified:—

Formic acid.	Propionic aldehyd.
Acetic acid.	Butyric aldehyd.
Propionic acid.	Benzoic acid.
Butyric acid.	Hydride of benzoyl.
Valeric acid.	Hydrocyanic acid.
Caproic acid.	Valeronitrile.
Acetic aldehyd.	

\* Globulin is not included in the remarks on the properties of the group; these observations only strictly apply to albumen, fibrin, and casein.

776. The albuminoids are insoluble in alcohol and ether, and are even precipitated from their aqueous solutions on the addition of alcohol to the liquid; the precipitate is generally insoluble in water after its precipitation by alcohol.

777. "These substances, either in their soluble or insoluble state, are readily dissolved by the aid of a gentle heat in a solution of KHO or NaHO, the addition of an acid to their alkaline solution so obtained causes the separation of a grayish flocculent precipitate, termed by Mulder protein, while a slight odor of  $H_2S$  is emitted, and a small quantity of phosphoric acid is also found in the solution. This precipitation is best effected by means of acetic acid, since the mineral acids are obstinately retained by the flocculi."—*Miller*.

778. In concentrated  $H_2SO_4$ , these substances dissolve with a brownish-red color.

779. Concentrated  $HNO_3$  produces in solutions of these substances a precipitate of a bright orange color, which gradually dissolves in the acid with effervescence;  $HNO_3$  added to the substances in the insoluble state colors them yellow and finally dissolves them. Mulder considers the yellow color to be due to the formation of a distinct compound which he has called *xanthoproteic acid*.

780. When to a solution of these substances concentrated HCl is added, and the solution is gently warmed, a white precipitate is first produced, which gradually dissolves, forming, if in contact with atmospheric air, a blue or violet-colored liquid. The reactions with  $HNO_3$  and HCl are very characteristic of the albuminoids.

781. Most acids produce a precipitate in solutions of these substances, but when they are added in excess redissolve the precipitate; when these acid solutions are diluted with a moderate quantity of water, a precipitate is formed which disappears on the further addition of water.

782. Metaphosphoric acid produces a precipitate in solutions of these substances, but an excess of the acid does not redissolve the precipitate.

783. Tannic acid produces a precipitate in solutions of these substances, and an excess of the acid does not redissolve the precipitate.

784. The acid solutions, but not the aqueous solutions, of the albuminoids give a precipitate with potassic ferrocyanide and ferricyanide; the next group of substances gives no precipitate with these reagents.

785. If a solution of Hg, prepared by dissolving two parts of it in four parts of  $\text{HNO}_3$ , of sp. gr. 1.40, be added to a solution of the albuminoids, or, if in the solid state, they are moistened with the Hg solutions, and the moistened solid or the fluid is then heated to a temperature from  $60^\circ$  to  $100^\circ$  C., an intense red color is produced, which is not destroyed by boiling water, nor by exposure to the air; the color is so intense that it may be perceived on adding the mercurial solution to a liquid containing not more than 1 part of albumen in 100,000 parts of water. The Hg solution gives a similar coloration with the members of the next group.

786. The aqueous solution of these bodies is precipitated by copper, lead, and mercury salts, the precipitate generally consists of the employed salt as well as the albuminoid.

787. If a solution of these substances be mixed with a solution of  $\text{CuSO}_4$ , and then a large excess of KHO be added, the greenish precipitate first formed is redissolved, and the liquid acquires a purple tint of great intensity and magnificence. The same reaction takes place with the next group of substances, and probably with any of the more complex nitrogenous substances.

788. In the living organism, fibrin, casein, and albumen are converted into one another; for example, the casein in milk, when this substance is used as food, must be converted in the animal economy into albumen and fibrin, and the two latter albuminoids must be converted into casein in the formation of milk. As the albuminoids have the same or nearly the same constitution, as shown by the following analyses, their conversion into one another can be easily accounted for. In the subjoined analyses, the ash has been deducted previous to calculating the composition in 100 parts:—

	Albumen.	Fibrin.	Casein.
Carbon . . . . .	58.3	58.0	58.83
Hydrogen . . . . .	7.2	6.9	7.15
Oxygen . . . . .	22.	23.5	22.52
Nitrogen . . . . .	15.7	15.4	15.65
Sulphur . . . . .	1.8	1.2	0.85
	100.0	100.0	100.00

789. The determination of the *rational formula* of bodies like the albuminoids is beset with difficulties; the difficulties

are so great with regard to these substances that they have not yet been overcome, and consequently their rational formula has not been determined. Different views have, however, been put forward to explain the relation between them, for, from their great similarity in composition and properties, there can be no doubt but that they are very closely related. The first view we shall notice is that of Mulder, as, although now abandoned, it is constantly referred to in works on the science; this view when first promulgated by the author was almost universally accepted by chemists, but they have long regarded it as erroneous.

790. Mulder considered that the flocculent precipitate obtained by adding an acid to an alkaline solution of the albuminoids was free from sulphur and phosphorus, and that this nitrogenized precipitate has identically the same composition, whether obtained from fibrin, albumen, or casein. This substance, which he called protein, he regarded as the fundamental principle of each of the albuminoids, and that albumen, fibrin, and casein were produced by the combination of different quantities of sulphur and phosphorus with protein; admitting this view of the construction of these bodies, it was easy to account for their conversion into one another, for the elimination or combination of small quantities of sulphur and phosphorus was all that was required to effect the change.

791. The so-called protein substance, Liebig has shown, is never obtained free from sulphur, that it always contains a small but variable quantity of this element; he considers that the precipitate is not a new and distinct substance, but that it is the original body slightly modified by the action of the potash.

792. "Gerhardt was of opinion that all the albuminoids are identical, not only in composition, but in chemical constitution, and that they differ from one another only in molecular arrangement, and by the nature of the mineral substances with which they are associated; in fact, that they contain a common proximate element, which, like many other organic compounds, is capable of existing in a soluble and an insoluble modification. Designating this common element by the name albumin, he supposed that white of egg and serum consist of acid albuminate of sodium, which is separated by heat into free albumin and neutral albuminate of sodium, the latter remaining dissolved; that casein, which is soluble and non-coagulated by heat, consists of neutral albuminate of potassium, from

which the organic compound may be precipitated by neutralizing the alkali with an acid ; and that fibrin is albumin in the insoluble state, more or less mixed with earthy phosphates. This view is in accordance with the fact that fibrin and casein may be dissolved in neutral potash salts (better with addition of a little caustic alkali), forming a liquid which coagulates by heat, and deflects the plane of polarization of a luminous ray to the left, like albumin ; and that fibrin and albumin, dissolved in a certain quantity of caustic alkali, exhibit the characters of soluble casein. Nevertheless, it is possible to obtain the albuminoids in some cases wholly, in others very nearly, free from mineral matters, and nevertheless exhibiting their distinguishing characteristics.

793. " Strecker supposes the albuminoids to be composed of a great number of radicles (a supposition in accordance with the variety of their products of decomposition), that the greater number of these radicals are the same in all, hence their great similarity ; but that each contains one or more such radicles peculiar to itself. Thus, when casein is converted in the animal body into albumen and fibrin, it may take the radicles required for that transformation from the other constituents of the milk, viz. the fat and the sugar."—Watts' "*Dictionary of Chemistry*."

## ALBUMEN.

794. *Properties of soluble Albumen*.—An aqueous solution of albumen is a tasteless, odorless, and colorless, but somewhat glairy liquid. It exerts a left-handed rotatory action upon a ray of polarized light. It is adhesive, and when spread on paper it forms when dried a varnished surface. Soluble albumen in the solid state is translucent and of a pale yellow color ; it is tasteless and odorless ; it swells in water, assuming a gelatinous appearance ; it does not dissolve freely in pure water, but very readily in water containing any alkaline salt.

795. If its aqueous solutions are evaporated to dryness at a temperature *not exceeding*  $49^{\circ}$  C., the solid albumen thus obtained will dissolve, though slowly, in water ; its solution is greatly promoted by the addition of NaCl or any salt of the alkalis ; a varying quantity of the albumen always becomes converted by the evaporation into the insoluble state.

796. If an aqueous solution of albumen is heated to about  $66^{\circ}$  C. it becomes opalescent, and at  $77^{\circ}$  C. it becomes entirely converted into the insoluble form. This conversion of the soluble into the insoluble form by heat, is the most characteristic property of albumen. The reason of the conversion is not known. Dumas thinks that it is probably a simple isomeric modification analogous to the conversion of cyanic into cyanuric acid.

797. *Action of alcohol, ether, etc., on soluble Albumen.*—Strong alcohol precipitates albumen from its solutions, and after its precipitation by this liquid it will not redissolve in water. If the alcohol is rendered slightly alkaline by KHO it causes no precipitate in solutions of albumen. Weak alcohol also precipitates albumen from its solution, but the precipitate redissolves completely in water.

798. *Ether*, if free from alcohol, only gelatinizes the albumen, it does not coagulate it.

799. *Kreasote* and *aniline* precipitate and coagulate it immediately.

800. *Rennet* does not precipitate it from its solutions. The *volatile* and *fixed* oils have no action upon it.

801. *Action of acids on soluble Albumen.*—The action of concentrated  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ , and  $\text{HNO}_3$  on albumen and the other albuminoids has already been noticed (778, 779, 780).

802. Dilute  $\text{H}_2\text{SO}_4$  produces no precipitate in solutions of albumen until the liquid is boiled.

803. Dilute  $\text{HCl}$  precipitates it at first, but afterwards redissolves it; this solution becomes milky on the addition of a little water; but if more water is added it becomes perfectly clear again.

804. Dilute  $\text{HNO}_3$  precipitates it readily and completely, and does not redissolve it; the precipitate is soluble in a large quantity of water. Dilute  $\text{HNO}_3$  is frequently employed as a test for the presence of albumen.

805. Metaphosphoric acid precipitates it immediately and completely. The ortho- and pyrophosphoric acids do not precipitate it.

806. The organic acids, tannic acid excepted (783), cause no precipitate in moderately concentrated solutions of albumen; its solutions, in the presence of organic acids do not coagulate by heat, but a pellicle gradually forms over the surface during evaporation.

807. Serum or white of egg mixed with a certain quantity of  $\text{NaCl}$ , or other salt of an alkali-metal, forms a liquid precipitable by phosphoric, acetic, tartaric, oxalic, and

lactic acids, etc.; conversely, a solution of albumen (or other albuminoidal substance) in acetic acid is precipitated by the salts of the alkali-metals. The precipitation is greatly facilitated by heat, and likewise takes place with greater facility as the proportion of salt added is greater. The precipitate dissolves in pure water, with greater facility in proportion as less heat has been applied in producing it; the solution is not coagulated by heat. It is soluble also in acetic acid, phosphoric acid, and even in alcohol, provided it has not been altered by desiccation, or by contact with the air. The aqueous solution is precipitated by certain salts, potassic ferrocyanide for example.

808. When a small quantity of acetic acid is added to white of egg or serum, so as just to saturate the alkali, and the liquid is then largely diluted with water; flocks of albumen are deposited after a while. If the supernatant liquid be then decanted, and the precipitate treated with a small quantity of solution of  $\text{KNO}_3$  or  $\text{NaCl}$ , it immediately dissolves, and the solution is coagulated on boiling.

809. *Dried soluble* albumen suspended in acetic, tartaric, or citric acid, swells up and is converted into coagulated albumen, which may be completely freed from acid by washing.

810. Cl and Br precipitate albumen from its solutions.

811. *Action of salts on soluble Albumen.*—"The greater number of the metallic salts, as iron, copper, lead, mercury, silver, antimony, aluminum, precipitate albumen; the precipitate consisting either of a combination of a basic salt with albumen, or a mixture of two compounds, one of which consists of the acid of the salt and albumen, and the other of the base of the salt and albumen. The albumen generally passes into the insoluble state in these combinations; the precipitate is generally soluble in an excess of serum or white of egg, and in some cases in the salt which produces it. Albumen, owing to its forming precipitates with them, is a valuable antidote in cases of poisoning by metallic salts.

812. " $\text{HgCl}_2$  is a delicate test of the presence of albumen, a liquid containing only a two-thousandth part of solid albumen is precipitated by it. The white precipitate formed is an insoluble compound of the salt with the organic substance; albumen, it is well known, is the antidote which is employed in this form of poisoning."

813. *The action of the alkalies and alkaline carbonates on soluble Albumen.*—"The presence of an alkali or an alkaline



carbonate, in a liquid containing albumen, greatly modifies the reactions of that substance; if the alkali is present in considerable quantities the solution does not coagulate by heat; but if it be evaporated, a pellicle forms over the surface similar in appearance to that produced upon a solution of casein by heat. Also, if to an alkaline solution of albumen, acetic, tartaric, or ortho-phosphoric acid, acids which in neutral or slightly alkaline solutions of albumen cause no precipitate, is added, a precipitate is produced which readily dissolves in an excess of the acid. These characters resemble those of casein, and some chemists have supposed that casein is simply an albuminate of potash.

814. If alcohol be added to an alkaline solution of albumen, it causes, as we have already noticed, no precipitate.

815. If a concentrated solution of KHO be added to a concentrated solution of albumen, albuminate of potash in the form of a gelatinous mass is produced; by washing the precipitate with cold water the greater part of the alkali can be removed, 5.4 per cent. of the alkali only remaining. If the gelatinous mass be washed with alcohol and then with water, it is insoluble in boiling alcohol and boiling water; but if it be washed with cold water, it is soluble in boiling water and boiling alcohol.

816. *Properties of insoluble Albumen.*—Insoluble albumen when moist appears as a white opaque elastic solid, it turns blue litmus *red*. When dried it is of a pale yellow color, and becomes brittle and translucent like horn. If the dried substance be immersed in water, it absorbs about four or five times its weight of water and regains the consistence of the undried substance. When coagulated albumen is boiled in water for about sixty hours in open vessels, it undergoes gradual decomposition, and a soluble compound is obtained which according to Mulder is teroxide of protein and ammonia. If heated to  $149^{\circ}$  C. with a small quantity of water in a sealed tube the albumen is redissolved, and furnishes a liquid which does not coagulate by heat, but which, when acidulated with acetic acid, gives a precipitate with potassic ferrocyanide.

817. *On the varieties of Albumen.*—"The properties of albumen vary in some degree with the source from which it is derived. The differences may in some cases be attributed to the presence of different mineral substances, but in others they are of such a nature as rather to point to the existence of different modifications of albumen.

Thus Frémy and Valenciennes have found that the albumen of the eggs of certain tribes of birds exhibits peculiar modifications. That from the eggs of different species of gallinaceous birds always exhibits the characters above described; but the eggs of swimming and wading birds yield an albumen which, when diluted with three measures of water, is not coagulated by heat, but is precipitated by  $\text{HNO}_3$ ; and the albumen from the eggs of predacious birds and some kinds of perching and climbing birds is neither coagulated by heat nor precipitated by nitric acid. The composition was, however, found to be the same in all cases.

818. "Blood-albumen exhibits the same reactions as that from white of egg, excepting that the latter when boiled gives up part of its sulphur in the form of sulphuretted hydrogen, which blood-albumen does not; nevertheless coagulated white of egg appears to contain more sulphur than blood-albumen.

819. "Scherer found in a liquid obtained from a case of ovarian dropsy a substance resembling albumin, but differing from it in not being completely precipitated by ebullition even after addition of acetic acid, and in dissolving in water after being precipitated by alcohol; this modification he named *Paralbumin*.

820. "*Metalbumin* is the name given by the same chemist to another supposed modification of albumin, likewise obtained from a pathological fluid, which exhibited similar peculiarities to the preceding, and was further distinguished by giving no precipitate with  $\text{HCl}$ , or with potassic ferrocyanide after acidulation with acetic acid."—*Watts' Dictionary of Chemistry*.

## FIBRIN.

821. Fibrin exists only in solution in the living plant or animal, for as soon as the solution is removed from the living organism it immediately begins to coagulate; this character distinguishes it from other analogous substances. The coagulation of the fibrin is prevented if the blood or other liquid containing the fibrin, at the moment it leaves the living organism, is mixed with solutions of certain salts, such as potassic carbonate or nitrate, sodic acetate, sulphate or chloride.

822. *Properties of Fibrin*.—Undried coagulated fibrin

appears in the form of long, white, elastic filaments, but when dried it forms a horny yellowish or gray solid. Both in the dried and undried state it is tasteless and insoluble both in hot and cold water, in alcohol, ether, etc. When long boiled, however, with water, it is, like albumen, gradually dissolved; by the exposure to heat and moisture it has evidently undergone decomposition, for the solution contains traces of ammonia. If undried fibrin is covered with water, it becomes in a few days viscid and acquires the odor of old cheese.

823. *Action of acids on Fibrin.*—The action of concentrated  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{HNO}_3$ , on fibrin and the other albuminoids has already been noticed (778, 779, 780).

824. When fibrin is immersed for about twelve hours in water slightly acidulated with  $\text{HCl}$ , it becomes gelatinous, and when this jelly is triturated with water, it yields a solution which coagulates by heat, is precipitated by potassic ferrocyanide, and affords a precipitate on the addition of  $\text{HCl}$ , not soluble except in an excess of this acid. According to Dumas and Cahours, water containing a millionth part of  $\text{HCl}$  or  $\text{HBr}$  gelatinizes fibrin, and if a few drops of gastric juice (pepsine) be then added, it is entirely dissolved in a couple of hours at a temperature of  $35^\circ$  to  $38^\circ \text{C}$ . Rennet produces the same effect.

825. Metaphosphoric acid does not dissolve fibrin. Orthophosphoric acid converts it into a gelatinous mass which is soluble in water, the fibrin is not precipitated from this solution on the further addition of the acid.

826. Concentrated acetic acid converts it into a gelatinous mass which is soluble in pure water.  $\text{H}_2\text{SO}_4$  and  $\text{HPO}_3$  precipitate it from this solution, the precipitate consisting of a compound of fibrin and the precipitating acid. Potassic ferrocyanide precipitates fibrin from its acetic solution. Alkalies also precipitate it, but it is redissolved by an excess of the alkali. According to Dumas the fibrin of young animals is more easily acted on by acetic acid than that of old ones, so that there is in this respect a material difference between the fibrin of veal and of beef.

827. *Action of the alkalies on Fibrin.*—Weak solutions of  $\text{KHO}$  and  $\text{NaHO}$  dissolve fibrin,  $\text{NH}_4\text{HO}$  exerts the same influence, but less rapidly; acetic and phosphoric acids and also the metallic salts precipitate fibrin, as they do albumen, from its alkaline solutions. Indeed an alkaline solution of fibrin resembles an alkaline solution of albumen in most of its characters.

## CASEIN.

828. *Properties of soluble Casein.*—Although this substance is met with in a state of solution in milk, it is doubtful whether it has a soluble form; it is considered that its soluble state in milk is due to a small quantity of free alkali; casein in solution does not coagulate by heat, the solution merely becomes covered with a film which is formed as often as it is removed. The casein of milk when obtained in the solid state does not redissolve completely in water.

829. *Action of alcohol, rennet, etc., on soluble Casein.*—Casein in solution is coagulated by alcohol, a portion at the same time entering into solution; a larger quantity is dissolved by boiling alcohol. The coagulum produced by absolute alcohol is insoluble in pure water; but the portion dissolved by alcohol is, after the removal of the alcohol, found to be still soluble in water.

830. Rennet (the inner membrane of the fourth stomach of the calf, salted and dried), or an infusion of it prepared at a low temperature, coagulates casein completely; this is the most remarkable and important mode of coagulating casein.

831. *Action of acids on Casein.*—The action of concentrated  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{HNO}_3$ , on fibrin and the other albuminoids has already been noticed (778, 779, 780).

832. Casein is precipitated from its solutions by all acids with the exception of carbonic acid, the precipitate redissolves in an excess of the acid; from its solution in acetic acid the mineral acids and potassic ferrocyanide precipitate it.

833. The coagulation of milk is due to the lactic acid, which is formed from lactine, neutralizing the alkali which renders the casein soluble, and thus causing that substance to pass into its insoluble state.

834. *Action of bases and of salts.*—"Coagulated casein is readily dissolved by solutions of the alkalies and of the alkaline carbonates; and if the solution be very feebly alkaline, the alkaline reaction may be completely neutralized by the casein. Solutions of  $\text{NaCl}$ , of  $\text{KNO}_3$ , and of  $\text{NH}_4\text{Cl}$ , likewise dissolve casein with facility, and these solutions, when evaporated by the aid of heat, become covered with an insoluble pellicle. Casein also unites with the alkaline earths and forms compounds which are inso-

luble in water. If a piece of poor cheese, which consists principally of casein, be reduced to a paste with water and mixed with  $\text{CaH}_2\text{O}_2$ , it produces a tenacious lute, which sets very hard, and may be used for cementing pieces of broken earthenware. In consequence of the tendency to the formation of these insoluble compounds, a solution of casein is precipitated by calcic salts or by  $\text{MgSO}_4$ , upon the application of heat to the mixture; this reaction is very characteristic of casein. Most of the metallic salts, such for instance as acetate and basic acetate of lead,  $\text{CuSO}_4$ ,  $\text{HgNO}_3$ , and  $\text{HgCl}_2$ , occasion precipitates in the cold with solutions of casein."—*Miller*.

### GLOBULIN.

835. Globulin occurs in the cells of the crystalline lens in a very concentrated solution; it was also considered to be present in red globules of Vertebrata, but later researches regard the two substances as distinct, the substance extracted from the blood is called Hæmatoglobulin or Hæmatocrystallin; it is decomposed by heat, by alcohol, by acids, and by alkalies into hæmatin and albumen.

836. Globulin is very similar to albumen in its properties, but it is distinguished from that substance by "its solutions not becoming opalescent at a lower temperature than  $73^\circ$ ; at  $83^\circ$  it assumes a milky turbidity, and at  $93^\circ$  C. separates as a milky coagulum which never becomes clear on filtration, and from which neither small quantities of acetic acid nor ammonia separate flakes capable of being removed by filtration; it is only when neutral alkaline salts are added, and the solution is then boiled, that the fluid becomes perfectly clear and flakes and small clots are deposited. The following reaction is very characteristic of globulin; its solution is not precipitated either by acetic acid or by ammonia, but it becomes strongly turbid when the fluid treated with acetic acid is neutralized with ammonia, or conversely when after the addition of ammonia it is neutralized with acetic acid. No other *soluble* albuminoid is precipitated both from its acid and its alkaline solution by neutralization, although almost all the *insoluble* albuminoids possess this property—a circumstance which affords a proof that globulin is reduced to the coagulated state both by an excess of alkali and by an excess of acid."—*Lehmann*.

837. *Vitellin*.—This name was given to the albuminous body of the yolk of egg; it is now known to be merely a mixture of albumin and casein.

838. *Recapitulation and remarks*.—This group of substances is distinguished from a large number of substances by containing nitrogen; the method for testing organic substances for this element is given at par. 749.

839. The substances forming this group are distinguished from a large number of organic substances containing nitrogen, by containing sulphur; the method for testing organic substances for this element is given at pars. 750 to 754. They are distinguished from the next group of substances by being precipitated from their acid solutions by potassic ferrocyanide.

840. Albumen is usually distinguished and separated from the other members of the group, by warming the fluid and coagulating; if the solution is alkaline it is necessary to neutralize it with acetic acid, care being taken not to add the acid in excess before warming the liquid; if the solution is very acid it ought to be neutralized, or the acid or alkaline liquid, instead of being neutralized, is treated with a strong saturated solution of  $\text{NH}_4\text{Cl}$ ; when  $\text{NH}_4\text{Cl}$  is employed, the solution requires a longer boiling in order to completely precipitate the albumen from the fluid than if it had been neutralized.

841. Fibrin is distinguished from the other albuminoids by the property which it possesses of coagulating spontaneously; it can exist only in the soluble form in the living plant or animal.

842. Casein in the absence of, or after the removal of, albumen, may be detected by adding to the solution  $\text{MgSO}_4$ , or  $\text{CaCl}_2$ , and then warming the solution; if casein is present a precipitate will be formed. But the test which distinguishes it from the other albuminoids is rennet; to render this test reliable, the rennet must be tolerably fresh, or at least free from all putridity; the mixture should be digested for a period not exceeding two hours, and at the temperature of  $40^\circ \text{C}$ .

## GELATIGENOUS GROUP.

## GELATIN. CHONDRIN.\*

843. *Properties of the group.*—Under the term gelatin we include the organic tissue of bone, cartilage, sinew, ligament, skin, cellular tissue, and serous membrane; all these substances dissolve by long-continued boiling in water, and the solution on cooling becomes a consistent gelatinous mass. It is represented in various degrees of purity by glue, size, and isinglass. Gelatin does not exist as *gelatin* in the animal tissues, but is formed from them by the action of boiling water. Müller has shown that there are two (if not three) distinct forms of gelatin. To that which is obtained from the permanent cartilages, the cornea, fungous bones, etc., the term *chondrin* is given, while *glutin* includes those forms of gelatin which are obtained from skin, serous membrane, hoof, bone, tendon, fibrous and spongy cartilage, cartilage of bone, etc.

844. The gelatigenous substances have hitherto been found only in animals. They contain a smaller amount of carbon and sulphur and a larger amount of nitrogen than the members of the albuminoid group, as will be seen on comparing the following table with the one given at par. 788.

	Chondrin.	Gelatin.
Carbon . . . .	49.97	50.40
Hydrogen . . . .	6.63	6.64
Nitrogen . . . .	14.44	18.34
Sulphur . . . .	0.88	} 24.62
Oxygen . . . .	28.58	
	<hr/> 100.00	<hr/> 100.00

845. The members of this group yield the same products as the members of the preceding group when treated with oxidizing agents, such as  $\text{MnO}_2$ , or  $\text{K}_2\text{Cr}_2\text{O}_7$ , and  $\text{H}_2\text{SO}_4$  (775).

846. These substances also give the same reaction as the members of the previous group with  $\text{HgNO}_3$ , par. 785.

847. The members of this group are especially distinguished by the following properties: they swell and become very translucent in cold water; they dissolve in hot water;

\* There are two other bodies known—Fibroin and Chitin—which belong to this group, but we have omitted them on account of their unimportance.

on cooling they separate as translucent masses, and are precipitated from the most dilute solutions by chlorine, tannic acid, and most of the salts of the earths and metals.

### GELATIN (Glutin).

848. Gelatin in a state of purity is a colorless transparent solid, which is hard, horny, and brittle; it is devoid of taste and smell, and has no action on vegetable colors. It is insoluble in alcohol and ether; it is insoluble in *cold* water, but softens and swells up in it; in *warm* water it dissolves, but the liquid as it cools becomes converted into jelly, gelatinizes, hence the name gelatine; 1 part of pure gelatin dissolved in about 80 parts of water, is sufficient to cause the liquid to gelatinize when it cools. If a solution of gelatin is boiled for a length of time, it does not gelatinize on cooling; the gelatin appears to be converted by the boiling into an isomeric modification which does not possess the property of gelatinizing.

849. Lime and lime phosphate are much more soluble in a solution of gelatin than in cold water. Common glue always contains a large quantity of lime phosphate, and this substance is considered by Mulder to be an essential constituent of gelatin, and it may be observed that chemical compounds of gelatin and lime phosphate can be prepared.

850. Moist gelatin exposed to the air rapidly putrefies; the liquid at first becomes highly acid, but afterwards gives off a large quantity of ammonia. This property of first becoming acid is characteristic of gelatin.

851. *Action of acids on Gelatin.*—Gelatin is soluble in all the dilute acids with the exception of tannic acid, and it is not precipitated from its solutions by any of the acids except tannic acid.

852. It is dissolved by concentrated  $\text{H}_2\text{SO}_4$  in the cold without change of color. The solution diluted with water and boiled, yields lencine, glycocine (sugar of gelatin), and some other products.

853. When gelatin is boiled with concentrated  $\text{HNO}_3$ , it becomes gradually converted into oxalic acid, saccharic acid and two substances resembling suet and tannic acid. When a solution of gelatin in dilute  $\text{HNO}_3$  is evaporated, nitrous gas is evolved, and the residue deflagrates just before dryness.

854. Tannic acid is a most delicate test of the presence of gelatin; when it is added to a solution of 1 part of gela-



tin in 5000 of water, a cloud is evident, and on adding the acid to a strong solution, a dense light colored precipitate is produced (tanno-gelatin), which is insoluble in water, alcohol, and ether, but soluble in a warm solution of potash. The composition of the precipitate does not appear to be constant. Tanno-gelatin is identical with *leather*.

855. *Action of chlorine*.—If Cl is passed through a solution of gelatin, a white pellicle forms round each bubble of the gas, and finally the whole of the gelatin is precipitated in the form of white elastic flakes or filaments. The precipitate is tasteless, slightly acid, imputrescible, insoluble in water and alcohol, but soluble in acids; its composition is not known. No similar substance is obtained by substituting Br or I for Cl.

856. *Action of the alkalis*.—A pure solution of gelatin is not precipitated by dilute solutions of the alkalis. When the gelatin solution is boiled with a concentrated solution of KHO it is decomposed into leucine, glycocine, and other products. The same change takes place when gelatin is carefully fused with solid KHO.

857. The solubility of lime and its phosphate in solutions of gelatin has already been noticed.

858. *Action of salts*.—"Lead, copper, aluminum, and iron salts, do not produce any precipitates in solutions of gelatin, but if a solution of KHO be added to the mixture of gelatin with alum, or with ferric sulphate, the basic aluminic or ferric sulphate which is formed carries down a large proportion of gelatin."

859.  $\text{HgCl}_2$  precipitates gelatin from its aqueous solution.

#### CHONDRIN.

860. Chondrin is transparent, horny, and glistening, it softens to a jelly in cold water, and in warm water it dissolves, but the liquid as it cools gelatinizes. It is insoluble in alcohol and ether. If a solution of chondrin be boiled for a length of time, it does not gelatinize on cooling.

861. *Action of acids*.—"Nearly all acids even organic acids, precipitate chondrin from its aqueous solution. The precipitate formed by hydrochloric, sulphuric nitric, phosphoric, phosphorous, chloric, or iodic acid, redissolves easily in excess of the acid; that formed by sulphurous, pyrophosphoric, hydrofluoric, carbonic, arsenic, acetic, tartaric, oxalic, citric, lactic, succinic or tannic acid does not redissolve in excess of the acid employed.

862. "Strong  $\text{H}_2\text{SO}_4$  dissolves chondrin, forming a syrupy liquid, which, when diluted with water and boiled, yields leucine without glycocine.  $\text{H}_2\text{SO}_3$  slowly decomposes chondrin.  $\text{HNO}_3$ , by prolonged action, converts it into xanthoproteic acid.

863. *Action of chlorine.*—"The aqueous solution of chondrin treated with  $\text{Cl}$  yields a precipitate.

864. *Action of salts.*—"Alum, aluminic sulphate, plumbic acetate and basic acetate, cupric sulphate, ferrous and ferric sulphates, ferric chloride, mercurous and mercuric nitrates, produce copious precipitates in a solution of chondrin, soluble for the most part in excess of the reagent. The precipitates formed by acetic acid, alum, and aluminic sulphate, dissolve completely on adding a sufficient quantity of potassic or sodic acetate, or of common salt. The precipitate formed by  $\text{Fe}_2\text{SO}_4$ , redissolves on heating the liquid.

865. " $\text{HgCl}_2$  does not precipitate a solution of chondrin; sometimes a slight turbidity is produced, owing apparently to the presence of a little gelatin."

866. *Recapitulation and remarks.*—"This group of substances is distinguished from a large number of organic substances by *containing nitrogen*. They are distinguished from the members of the preceding group by potassic ferrocyanide producing no precipitate in their solutions. And their peculiar behavior with water at once distinguishes them from all other substances.

867. Gelatin is distinguished from chondrin by giving a precipitate with  $\text{HgCl}_2$ .

868. Chondrin is distinguished from gelatin by being coagulated by the vegetable acids such as acetic acid; as well as by alum, and by the neutral and basic lead acetates.

## SUGARS.

### MILK-SUGAR, GRAPE-SUGAR (Glucose), INOSITE.

869. As milk-sugar, glucose, and inosite, are the chief varieties of sugar met with in the animal kingdom, they are the only sugars we shall notice in this part of the work.

870. The sugars are all soluble in both cold and warm water, but they are more soluble in hot water than cold. They all possess a sweet taste; but there are great differences in the relative sweetness of the different varieties.

Sugar of milk (Lactin, Lactose)  $C_{12}H_{22}O_{11}H_2O$ .

871. This variety of sugar is an animal product, it is found only in the milk of the mammalia, and is the substance which gives the sweet taste to fresh milk. It forms white, translucent four-sided prisms, of great hardness. It is soluble in about six parts of cold, and two parts of boiling water; it does not form a syrup, and has only a feeble sweet taste. It is insoluble in alcohol and ether. Its aqueous solution produces right-handed rotation of a ray of polarized light.

872. It is converted into glucose when boiled with dilute acids.  $HNO_3$  converts it into mucic acid, with a little oxalic acid; it differs from the other sugars, and resembles the gums in furnishing these acids by the action of  $HNO_3$  upon it.

873. It becomes gradually converted in milk, from the influence of the caseous matter, into lactic acid, thus:— $C_{12}H_{22}O_{11}H_2O = 4(H_2C_3H_4O_3)$ .

874. Milk-sugar reacts with  $CuSO_4$  and  $KHO$ , exactly in the same manner as glucose (880).

Grape or Starch Sugar, *Glucose*,  $C_6H_{12}O_6H_2O$ .

875. Grape-sugar abounds in grapes, figs, plums, and other fruits; it is also formed from starch, cane-sugar, and woody fibre, by processes which will be described under Vegetable Chemistry. It is also a morbid constituent of the urine in the disease called *diabetes*, its appearance in the urine is the most characteristic feature of the disease.

876. "Glucose crystallizes with difficulty in warty concretions, composed of hard transparent cubes. It forms with  $NaCl$  a compound that crystallizes with facility, which is a distinctive character of this variety of saccharine matter.

877. "Glucose is distinguished from cane-sugar by several characters; it is considerably less soluble in water than cane-sugar, though it is more readily taken up by alcohol, and crystallizes from a hot solution of alcohol containing not more than 5 per cent. of water in anhydrous prisms ( $C_6H_{12}O_6$ ). It requires nearly two and a half parts of glucose to produce the same sweetening effect as is produced by one part of cane-sugar. The action of  $H_2SO_4$  upon grape-sugar is quite different from its action upon cane-sugar, as, instead of charring and destroying it as it does cane-sugar, it forms with it a definite compound acid, the solution of which is pale yellow; this acid has been termed sulphosaccharic acid" ( $C_6H_{12}O_5SO_3$ ).

878. Grape-sugar is resolved in contact with yeast or other ferments into alcohol, carbonic acid and water: thus—  

$$\text{C}_6\text{H}_{12}\text{O}_6\text{H}_2\text{O} = 2\text{C}_2\text{H}_5\text{O} + 2\text{CO}_2 + \text{H}_2\text{O}.$$

879. When a solution of grape-sugar is heated with a solution of one of the fixed alkalies it is rapidly decomposed, which is evidenced by the fact that the liquid darkens in color and finally becomes nearly black. This action of the fixed alkalies on grape-sugar has been proposed as a test for sugar in urine; it is called Moore's test, and is employed as follows: To the suspected urine, an equal bulk of the ordinary solution of KHO is to be added and the whole boiled gently for about five minutes; a deep orange-brown or black color will be produced if sugar is present. This ought only to be employed as a confirmatory test, as in many cases it might prove very fallacious.

880. The dark brown substance (melassic acid), which is produced when an alkaline solution of sugar is heated, has a very powerful affinity for oxygen, it speedily reduces CuO black oxide to  $\text{Cu}_2\text{O}$  the red oxide when a cupric salt is added to the alkaline solution of sugar. On this property is founded the most valuable chemical test for sugar which we possess; this is known as Trommer's test. The simplest plan of employing this test is to add a solution of KHO in tolerable excess,\* if a precipitate is produced, as is frequently the case in urine, filter and to the filtrate (in a test-tube) add a few drops of a *very dilute* solution of  $\text{CuSO}_4$ .† If sugar is present, the precipitate which first forms is redissolved on shaking, and the fluid becomes of a clear blue color. This blue solution is then heated to boiling, whereon a yellow cloud (hydrated  $\text{Cu}_2\text{O}$ ) forms, which speedily changes to a *red* (the anhydrous  $\text{Cu}_2\text{O}$ ) precipitate.

881. When testing urine for sugar by this method the mixture of urine and KHO should not be warmed before the addition of the copper solution, and it ought only to be boiled gently for a minute or two, as several substances besides sugar separate  $\text{Cu}_2\text{O}$  from alkaline solutions of copper if the boiling is prolonged. A counter experiment ought

\* An excess of KHO is productive of no harm.

† The solution of the copper salt ought to be so dilute as only to have a faintly blue tinge. Instead of cupric sulphate, Drs. Taylor and Brande recommend cupric tartrate, which is certainly to be preferred to the sulphate; they recommend recently precipitated cupric tartrate to be dissolved in a solution of NaHO or  $\text{Na}_2\text{CO}_3$ . Cupric tartrate is more easily decomposed than the sulphate, less boiling is therefore required, which is a great advantage.

therefore always to be made by leaving at rest one-half the mixture of urine, potash, and copper solution, *before it has been warmed*, for six to twenty-four hours without being heated, if sugar is present in the urine a separation of  $\text{Cu}_2\text{O}$  will also take place in this mixture. Sugar is the only substance which can be present in the urine which reduces the copper salt without heat.

882. *Fermentation test.*—Fermentation is frequently employed as a test for the presence of sugar. “When used merely as a qualitative test to indicate whether sugar is or is not present in urine, the following is the simplest way of applying it. Fill a test-tube with the suspected urine, having previously mixed with it a few drops of fresh yeast, or still better, a little of the dried German yeast; close the open end with a small saucer or evaporating dish, and while gently pressing the latter upon the tube invert them. A little more of the urine is then poured into the saucer in order to prevent the escape of any of the liquid from the tube, and if any bubbles of air have accidentally been allowed to enter, the exact height of the upper surface of the liquid in the tube must be marked with ink or with a strip of gummed paper. The tube with its contents is then set aside in a warm place having a temperature of about  $21^\circ$  or  $27^\circ\text{C}$ ., for 24 hours. If sugar is present it begins almost immediately to undergo the vinous fermentation, the  $\text{CO}_2$  as it is formed rises in minute bubbles, causing gradual and gentle effervescence, and collects in the upper tube, displacing an equal volume of liquid which escapes through the open end of the tube into the saucer. When the quantity of sugar present is at all considerable, the urine, after fermentation, will be found to possess a faint vinous smell. As bubbles of gas are sometimes given off by the yeast itself, it is a good precaution to put the same quantity of yeast into a second tube of equal size, and fill it up with pure water. The amount of gas, if any, derived from the yeast will thus be rendered apparent, and may afterwards be detected from the volume of gas in the tube containing the urine.”—*Bowman*.

Inosite or Phaseomannite  $\text{C}_6\text{H}_{12}\text{O}_5, 2\text{H}_2\text{O}$ .

883. “This sugar occurs in almost all parts of the animal system and is identical with phaseomannite, which occurs in unripe beans, and in many other plants. It forms prismatic crystals of the form of gypsum; it is soluble in water, but insoluble in alcohol and ether; it has a sweet

taste; and is not susceptible of the vinous fermentation, but with chalk and cheese it yields lactic and butyric acids. It does not reduce cupric salts. If it be evaporated with  $\text{HNO}_3$  nearly to dryness, and then mixed with a little  $\text{NH}_4\text{HO}$  and  $\text{CaCl}_2$ , and again evaporated, a beautiful rose tint is produced, which is quite characteristic of it."

## ALKALOIDS.

### UREA, CREATININE, CREATIN.

884. The only bodies we shall notice belonging to this class are the three given in the list; creatin is neutral to test-paper, but it has been combined with acids, and has the characters of a weak base. It will be seen that it is closely connected with creatinine. The three substances possess no marked properties which are common to the three.

### UREA ( $\text{CH}_4\text{N}_2\text{O}$ ).

885. "This important compound is an essential constituent of the urine of animals; it is abundant in that of the mammalia and particularly so in the urine of the carnivora; but it has also been met with in the urine of birds and of amphibia. Urea is the principal outlet for the nitrogen of the system, after the materials which compose the animal tissues have experienced oxidation under the influence of the respired air, a healthy human adult excreting about an ounce of urea daily. Urea is not formed in the kidneys; these glands appearing to act somewhat in the manner of filters, by means of which the urea is separated from the mass of the blood, in which it exists already formed before reaching the kidneys."—*Miller*.

886. Urea can be formed *artificially* in a variety of ways; one of the simplest methods for its formation is by evaporating ammoniac cyanate ( $\text{NH}_4\text{CNO}$ ), which is metameric with urea, at a gentle heat; by a mere alteration of the elements of ammoniac cyanate urea is formed as shown in the following equation:  $\text{NH}_4\text{CNO} = \text{CH}_4\text{N}_2\text{O}$ .

887. Urea is formed whenever cyanic acid or cyanates come in contact with ammonia or ammoniac salts. It is also formed by the spontaneous decomposition of an aqueous solution of cyanogen. Ammoniac cyanate is first formed, and this body becomes converted into urea as the liquid

evaporates. It is also formed when ammonia is acted upon by phosgene gas ( $\text{COCl}_2$ ).

888. Béchamp has recently succeeded in preparing urea from albumen, by subjecting it to the oxidizing action of potassic permanganate.

889. "A solution of urea, *if pure*, may be kept at ordinary temperatures *without alteration*, and it may even be boiled without undergoing decomposition; but if heated in a sealed tube to about  $100^\circ$ , it combines with four equivalents of water and is converted into ammonic carbonate— $\text{CH}_4\text{N}_2\text{O} + 2\text{H}_2\text{O} = (\text{NH}_4)_2\text{CO}_3$ . The same change takes place slowly at ordinary temperatures in the presence of the mucus of the bladder, the ammoniacal odor acquired by urine after keeping it for a few days being due to this alteration. A similar decomposition into carbonic acid and ammonia occurs when urea is fused with KHO or treated with concentrated  $\text{H}_2\text{SO}_4$ .

890. Cl, when transmitted into an aqueous solution of urea, resolves it into  $\text{CO}_2$  and N and HCl: thus,  $2\text{CHN}_2\text{O} + 2\text{H}_2\text{O} + 3\text{Cl}_2 = 2\text{CO}_2 + 2\text{N}_2 + 6\text{HCl}$ .

891. Nitrous acid decomposes urea immediately into  $\text{CO}_2$ , N, and  $\text{H}_2\text{O}$ :  $\text{CH}_4\text{N}_2\text{O} + 2\text{HNO}_2 = \text{CO}_2 + 2\text{N}_2 + 3\text{H}_2\text{O}$ .

892. Urea crystallizes in flattened four-sided prisms; they generally resemble  $\text{KNO}_3$  in appearance, and have a similar cooling, saline taste; they are inodorous. They are soluble in their own weight of cold water and in every proportion in hot water; they dissolve in 4.5 of cold and in two parts of boiling alcohol; but they are insoluble in ether, and in an excess of strong nitric acid. Its solution is neutral to test-paper.

893. Urea is basic in its characters, although neutral to test-paper; it combines with acids to form salts, some of which are crystalline. "Of these, the two which are of the most practical importance, are the oxalate ( $2\text{CH}_4\text{N}_2\text{O}$ ,  $\text{H}_2\text{C}_2\text{O}_4$ ), and the nitrate ( $\text{CH}_4\text{N}_2\text{O}$ ,  $\text{HNO}_3$ ), which, on account of their sparing solubility in water, supply a ready means of separating urea from the other matters coexisting in the urine.

894. "*Oxalate of urea* may be prepared by concentrating urine on a water-bath to about one-eighth of its bulk, and filtering through muslin, in order to separate the insoluble sediment of phosphates and urates, which are gradually deposited during the evaporation. The liquid thus clarified is mixed with about an equal bulk of a strong solution of oxalic acid in hot water, or the solid acid in powder may

be added as long as the liquid, heated to about  $88^{\circ}$  or  $94^{\circ}$  C., continues to dissolve it. The mixture, on cooling, deposits an abundant crop of crystals of oxalate of urea, mixed with a little of the excess of oxalic acid, and colored brown by the adhering impurities. The crystals are then gently pressed between folds of filtering paper, washed with a small quantity of ice-cold water, and purified by recrystallization; the last traces of coloring matter being removed, if necessary, by boiling the solution with animal charcoal. The oxalate thus obtained is colorless, and in the form of tabular or prismatic crystals, which are readily soluble in hot water, but only sparingly so in cold, 25 parts of which dissolve not more than 1 part of the salt.

895. "*Nitrate of urea* may be obtained by adding strong colorless  $\text{HNO}_3$ , free from  $\text{HNO}_2$  (891), to urine previously concentrated by evaporation to about one-third its bulk; the nitrate gradually separates in irregular rhomboidal plates, more or less colored and modified in form by the impurities present. The crystals are washed with a little ice-cold water, then pressed between folds of filtering paper, and redissolved in lukewarm water; lastly, they are purified by recrystallization, and, if necessary, the last traces of coloring matter may be removed by boiling the solution with animal charcoal. It is soluble in about 8 times its weight of cold water, and in a much smaller quantity of hot. It is tolerably soluble also in alcohol, especially when warm, but almost insoluble in ether.

896. "The formation of this crystalline compound on the addition of  $\text{HNO}_3$ , is one of the most distinctive tests for the presence of urea which we possess. The experiment is made easily, and with great delicacy, under the microscope, by concentrating a drop or two of urine on a glass slide, and adding to it about an equal quantity of pure  $\text{HNO}_3$ ; the nitrate will gradually crystallize in delicate rhomboidal plates, the number and abundance of which will furnish some indication of the quantity of urea present in the secretion."\*

### CREATININE ( $\text{C}_4\text{H}_7\text{N}_3\text{O}$ ).

897. This substance is a powerful organic base; its aqueous solution restores the blue color to reddened litmus

\* Bowman's Medical Chemistry.



paper, and when heated with solutions of ammoniac salts it expels the ammonia like the fixed inorganic alkalies. It forms colorless prismatic crystals, and its salts are also crystalline. It dissolves in about 12 parts of cold water; it is much more soluble in hot water; it is very soluble in boiling alcohol, but much less so in cold alcohol, it therefore crystallizes out as the boiling solution cools.

898. It has a strong tendency to form basic double salts; example: if a solution of  $\text{AgNO}_3$ , moderately concentrated, be mixed with one of creatinine, it becomes converted into a magma of white needles, which are very soluble in boiling water, and it forms a similar compound with a solution of  $\text{HgCl}_2$ . On the addition of a concentrated solution of  $\text{ZnCl}_2$  to a solution of this base, a double compound  $(\text{C}_4\text{H}_7\text{N}_3\text{O})_2\text{ZnCl}_2$  is precipitated in a crystalline form; when very slowly formed the crystals are distinctly prismatic, but when quickly produced, and as seen under the microscope, fine needles are observed concentrically grouped together, forming either perfect rosettes, or tufts which cross each other, or of which each two are connected by thin short stalks, so as to resemble brushes passing one into the other. As  $\text{ZnCl}_2$  is the test usually employed to detect this base, it is important to observe that the double compound of zinc and creatinine is not precipitated on the addition of the zinc chloride to the creatinine chloride; but that the separation at once takes place, if before the addition of the  $\text{ZnCl}_2$  solution, a sufficiency of sodic acetate is mixed with the creatinine salt.

899. This base has been found in the juice of muscle, in the blood as well as in the urine. Creatin is converted into creatinine by the action of strong acids.

#### CREATIN ( $\text{C}_4\text{H}_9\text{N}_3\text{O}_2 \cdot 2\text{H}_2\text{O}$ ).

900. In its pure state, this substance forms brilliant, colorless, prismatic crystals, which become dull by loss of water at  $100^\circ \text{C}$ . It has a bitter, pungent taste. It dissolves in 75 parts of cold water. Boiling water takes up a much larger quantity of it, but, as it cools, the creatin separates in the crystalline form. Alcohol takes up only one part in 9410 parts; and in ether it is completely insoluble. In an impure state the solution readily putrefies.

901. It dissolves without change in dilute mineral acids; but when boiled with concentrated acids, it gives off water,

and is converted into creatinine:  $\text{C}_4\text{H}_9\text{N}_3\text{O}_2 \cdot 2\text{H}_2\text{O} - 3\text{H}_2\text{O} = \text{C}_4\text{H}_7\text{N}_3\text{O}$ .

902.  $\text{ZnCl}_2$  produces no precipitate with perfectly pure creatin; but, if creatinine is present, a triple compound consisting of chloride of zinc, creatin, and creatinine, is precipitated in the form of radiating crystals.

903. This substance is found in the juice of muscles; and it is also found in the urine.

## ACIDS.

LACTIC ACID, HIPPURIC ACID, GLYCOCHOLIC ACID, HYOCHOLIC ACID, TAUROCHOLIC ACID.

904. These acids are grouped together simply on account of their acid character.

### LACTIC ACID $\text{H}_3\text{C}_3\text{H}_4\text{O}_3$ .

905. There are two modifications of this acid, the one called *ordinary* lactic acid is formed by the fermentation of milk, cane, and grape sugars; it is also found in vegetable matters which have turned sour. The other modification, called *sarcolactic* or *paralactic* acid, exists in muscular flesh.

906. The ordinary lactic acid, in its most concentrated state, is a colorless, inodorous, thick, syrupy fluid, which cannot be solidified by the most intense cold; its specific gravity = 1.215, it dissolves readily in water, alcohol, and ether, attracts water from the atmosphere, has a strongly acid taste and reaction, decomposes when heated, and displaces not only volatile acids, but even many of the stronger mineral acids from their salts.

907. With bases lactic acid generally forms neutral salts, all of which are soluble in water, and many in alcohol, but none in ether. Most of the lactates may be heated to  $150^\circ$  or  $170^\circ$ , and some even to  $210^\circ$ , without undergoing decomposition.

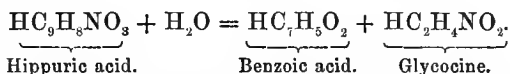
908. Sarcolactic acid is hardly distinguishable from ordinary lactic acid; the difference between the two is mostly distinctly marked in the calcic and zinc salts. If sarcolactic acid be heated for a long time to  $130^\circ$  or  $140^\circ$ , it is converted into the anhydride, which, when boiled with water, is converted into ordinary lactic acid.

HIPPURIC ACID OR BENZAMIDACETIC ACID,  $\text{HC}_9\text{H}_8\text{NO}_3$ .

909. This acid occurs in combination with K or Na in large quantity in the urine of herbivorous animals, and in smaller quantity also in human urine.

910. This acid, when treated with nitrous acid, undergoes the decomposition peculiar to amidogen compounds, viz., the formation of a non-nitrogenous acid, water, and the liberation of nitrogen. The acid formed on treating hippuric acid with nitrous acid is benzo-glycolic acid ( $\text{C}_9\text{H}_8\text{O}_4$ ). Under the influence of boiling water, benzo-glycolic splits up into benzoic and glycolic (oxyacetic) acids.

911. When hippuric acid is boiled for some hours with concentrated HCl, it assimilates the elements of water, and is resolved into benzoic acid and amidacetic acid or glycocine:—



912. Hippuric acid has been artificially made by acting upon the zinc salt of glycocine with chloride of benzoyl:—



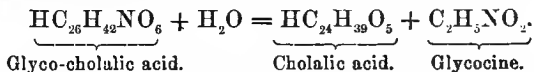
913. This acid crystallizes in rhomboidal prisms, or in thin plates. It is sparingly soluble in cold water, one part requiring 400 parts for its solution; but it is very freely soluble in hot water. It is readily soluble in alcohol; but only sparingly soluble in ether, which distinguishes it from benzoic acid (579). Exposed to a high temperature it is decomposed into hydrocyanic acid, benzoic acid, ammoniac benzoate, and other products. Heated with a fragment of KHO it disengages  $\text{NH}_3$ . If placed in contact with ferments, it undergoes a kind of fermentation, the products of which are benzoic acid and ammonia.

914. Owing to this speedy conversion of it into benzoic acid and ammonia by ferments, it is not surprising that if the urine becomes in the slightest degree putrid, it is speedily decomposed into benzoic acid and ammonia. On the other hand, when benzoic acid is taken into the system, it is converted into hippuric acid, and is found in the urine in that state.

GLYCO-CHOLALIC ACID OR GLYCOCHOLIC ACID (*Cholic acid* of Strecker)  $\text{HC}_{26}\text{H}_{42}\text{NO}_6$ .

915. This acid, in combination with the fixed alkalies, exists in the bile of man and other animals, but it is present in the greatest quantity in ox-bile. The acid is a white crystalline solid; it has a strong acid reaction, and a bitterish-sweet taste. It is more soluble in hot water than cold; alcohol dissolves it freely, but leaves it as a resinous mass on evaporation; it is very sparingly soluble in ether. The salts which it forms with the alkalies and alkaline earths may be crystallized; they are soluble in alcohol.

916. When this acid is boiled with an alkaline solution, as solution of  $\text{KHO}$  or  $\text{BaH}_2\text{O}$ , it is decomposed into glycocine (amidacetic acid), and a non-nitrogenous acid, called cholalic acid\* (the cholic acid of Demarcay):—

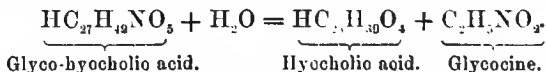


917. When it is boiled with concentrated  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$ , it is split up into glycocine and choloidinic acid ( $\text{C}_{24}\text{H}_{38}\text{O}_4$  = cholalic acid—1 eq. of water); if the ebullition with the acids be continued, the choloidinic acid is decomposed into a resinous substance, called, from its insolubility in water, *dyslysin* ( $\text{C}_{24}\text{H}_{38}\text{O}_3$ ), and water.

GLYCO-HYCHOLIC ACID,  $\text{HC}_{27}\text{H}_{42}\text{NO}_5$ .

918. Pig's bile differs from the bile of other animals, inasmuch as it contains glyco-hyocholic acid instead of glyco-cholalic acid; the former acid is decomposed like the latter by alkaline solutions and acids and into substances of analogous composition.

919. When it is boiled with an alkaline solution, it is decomposed for instance into glycocine and hyocholic acid:—



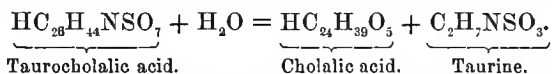
920. When it is boiled with acids it is decomposed into glycocine and a substance homologous with dyslysin, which is termed hyodyslysin ( $\text{C}_{25}\text{H}_{38}\text{O}_3$ ).

\* This acid is soluble in  $\text{H}_2\text{SO}_4$ , and on the addition of a drop of this acid and a solution of sugar (one part of sugar to four of water) a purple violet color is produced which constitutes Pettenkofer's test for bile.

TAUROCHOLALIC ACID OR TAUROCHOLIC ACID (*Choleic Acid of Strecker*)  $\text{HC}_{26}\text{H}_{44}\text{NSO}_7$ .

921. The bile of man and most animals, with the exception of the ox and pig, consists mainly of taurocholalate of soda or potash. The alkaline salts of this acid are very soluble in water and alcohol. They give no precipitate with neutral lead salts, but with the basic salts they deposit a plaster-like compound, which is soluble in boiling water. They yield with  $\text{H}_2\text{SO}_4$  and sugar a violet color similar to that produced by the cholates.

922. When this acid is boiled with alkaline solutions it is decomposed into cholalic acid and taurine:—



923. When it is boiled with acids it is decomposed into taurine\* and choloidinic acid or dyslysin, according to the duration of the experiment (917).

CYSTINE, XANTHINE, AND CHOLESTRIN.

924. These three substances are met with in *calculi*.

925. CYSTINE OR CYSTIC OXIDE ( $\text{C}_3\text{H}_7\text{NSO}_2$ ). This substance is met with nowhere but in the urine; it was originally discovered by Wollaston in a urinary calculus; calculi of this nature, although very rare, have since been found by many other chemists. "It occurs in colorless, transparent, hexagonal plates or prisms; it is devoid of taste and smell, and is insoluble in water and alcohol. It dissolves in oxalic and the mineral acids, forming with them saline combinations, most of which are crystallizable, but it does not unite with acetic, tartaric, or citric acid; it is decomposed by nitric acid, leaving, on the evaporation of the fluid, a reddish-brown mass; it dissolves freely in the caustic fixed alkalies and their carbonates. It dissolves in  $\text{NH}_4\text{HO}$ , but does not unite with it, so that on evaporation it crystallizes unchanged. It is insoluble in  $(\text{NH}_4)_2\text{CO}_3$ ; hence it is best precipitated from its acid solutions by  $(\text{NH}_4)_2\text{CO}_3$ , and from its alkaline solutions by acetic acid.

\* The student is referred to the author's "Second Step in Chemistry," page 525, for an account of Kolbe's important experiments on the constitution of taurine.

926. "Cystine does not fuse on the application of heat, but it burns with a *bluish-green flame*, developing at the same time a very peculiar acid odor; on dry distillation it develops a stinking empyreuma and ammonia, and leaves a voluminous porous coal. On boiling it with alkalis, ammonia is first developed, and subsequently an easily inflammable gas, which burns with a blue flame.

927. "Cystine is characterized by the readiness with which it crystallizes in well-formed hexagonal plates, which may be distinguished with great ease under the microscope, and by its solubility both in alkalis and mineral acids. Further, it may be known by the peculiar odor which it develops on dry distillation and on burning, which is unlike that evolved by any other similar substance. Liebig has given the following test for cystine. The potash-extract of the substance in which we are searching for cystine must be decomposed with a solution of  $\text{PbO}$  in  $\text{KHO}$ ; if, on the application of heat, there be a precipitation of  $\text{PbS}$ , cystine is probably present; we must, however, previously satisfy ourselves that no other organic substance containing sulphur, as for instance, albumen, mucus, etc., be simultaneously present.

928. "If cystine be mixed with a small quantity of the urates, the two substances may be separated by the aid of boiling water, in which the former is insoluble. Uric acid occasionally appears under the microscope in the form of hexagonal tablets, but we should never trust in these cases to microscope examinations."—*Lehmann*.

929. XANTHINE or XANTHIC OXIDE ( $\text{C}_5\text{H}_4\text{N}_4\text{O}_2$ ). This substance has also been named *uric oxide* and *urous acid*, owing to its being regarded as uric acid in a lower stage of oxidation. It is the principal constituent of a very rare variety of urinary calculus. It is one of the products in the decomposition of guanine, a substance found in guano and in the excrement of the garden spider. It is likewise present in nearly every part of the animal organism, and, although in very minute quantities, in urine. It is a white amorphous powder, and it acquires a waxy lustre on friction with a hard body. It is very slightly soluble in water; it is insoluble in alcohol and ether. It dissolves easily in ammonia. It also dissolves freely in the fixed alkalis; carbonic acid separates it from its alkaline solution. It is all but insoluble in  $\text{HCl}$  and  $\text{H}_2\text{C}_2\text{O}_4$ ; it is soluble in  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ . It dissolves in  $\text{HNO}_3$  without disengagement of gas, and gives on evaporation a yellow residue,

which, on addition of  $\text{NH}_4\text{HO}$  or  $\text{KHO}$ , turns yellowish-red. From the circumstances under which it occurs it can only be confounded with cystine or uric acid; it differs from these by its amorphous condition. It is distinguished from cystine by its insolubility in  $\text{HCl}$  and  $\text{H}_2\text{C}_2\text{O}_4$ . It is distinguished from uric acid by its solubility in  $\text{NH}_4\text{HO}$ , and by the residue obtained on evaporating its  $\text{HNO}_3$  solution not turning red on the addition of  $\text{NH}_4\text{HO}$  (617).

930. **CHOLESTRIN**  $\text{C}_{26}\text{H}_{44}\text{O}$ .—"This substance is found in small quantity in various parts of the animal system, as in the bile, in the brain and nerves, and in the blood. It forms the chief ingredient of *biliary calculi*, from which it is easily extracted by boiling the powdered gall-stones in strong alcohol, and filtering the solution while hot; on cooling the cholestrin crystallizes in brilliant colorless plates. It has the physical characters of a fat, is insoluble in water, tasteless and inodorous; it is freely soluble in boiling spirit and also in ether. It is not saponified by potash; thus differing from other fatty and oily substances which it resembles in many respects. It melts at  $137^\circ$ , and sublimates at  $200^\circ \text{C}$ ."

## COLORING MATTERS

931. We group together the coloring matter of the urine, the bile, and the blood.

932. *Coloring matter of the urine*.—"The coloring matter of the urine is constantly undergoing change; by means of neutral and basic lead acetate it may be separated into two substances which contain different amounts of carbon. The substance which contains most carbon may be obtained as a dark-blue powder; when dry it has a copper color like indigo and dissolves in alcohol, giving a purple-blue solution. It is said to occur most evidently in Bright's disease. Virchow states that he met with this blue pigment in crystals in unhealthy urine." Thudicum believes there is only one *normal* urinary pigment which he has named *urochrome*, an amorphous substance of a pure yellow color; Schunk believes there are two.

933. *Coloring matter of the bile*.—"The principal coloring matter of the bile has been called *cholepyrrhin* or *bilirubine* ( $\text{C}_{16}\text{H}_{15}\text{N}_2\text{O}_3$ ). When dry it is reddish-brown and uncrystallizable, insoluble in water, slightly soluble in alcohol and ether, easily soluble in chloroform and in solutions of

the alkalies. The color of these solutions is yellow or orange; if to the alkaline solution is added an equal volume of alcohol and then fuming nitric acid charged with nitrous vapors, it passes through *green, blue, violet, and red*; after some time it again turns yellow; this reaction is very delicate.

934. Another coloring matter has been called *biliverdin*. It is dark green, amorphous, without taste or smell, insoluble in water, slightly soluble in alcohol, but soluble in ether.

935. *Coloring matter of the blood*.—The red coloring matter of the blood-corpuscles is called hæmatin or hæmatosin; it leaves when burnt a residue of ferric oxide and calcic phosphate. It is unaffected by dilute  $\text{NH}_4\text{HO}$ , but is entirely destroyed by ebullition, with the formation of a dirty-colored coagulum, which dissolves in KHO with an indistinct greenish color.

936. *Tests for blood*.—"Blood-stains on articles of clothing may be identified—1. By their peculiar crimson-red color. 2. By the shining and raised surface of the stain or spot (dried albumen and fibrin). 3. By their ready solubility in water to which they give a red color. The water under these circumstances contains albumen as well as hæmatosin. Weak ammonia does not change the red color to a *blue, green, or crimson* tint. When boiled, the albumen and hæmatosin are both coagulated, and the red color is entirely destroyed; a muddy brown coagulum subsides which is quite insoluble in water and alcohol." 4. Bloxam has proposed the following test, which is very delicate. A mixture of tincture of guaiacum and oxonized ether (that is a solution of hydric peroxide ( $\text{H}_2\text{O}_2$ ) in ether); this mixture instantly produces with blood or blood-stains a beautiful *blue tint*. For the examination of such stains in a dry state, an inch power of the microscope will be found convenient.

937. "By employing a small quantity of water on a glass slide in order to dissolve the stain, the clot may be broken up and the red corpuscles separated. These may be examined by a quarter-inch power under the microscope. When detected, the evidence of the presence of blood is placed beyond doubt. No other red coloring matter, vegetable or animal, owes its color to corpuscles or cells. A small quantity of glycerine added to the water which is used as a solvent prevents it from drying too rapidly."—*Brande and Taylor*.



938. *Test for bile.*—Bile is essentially composed of soda salts of the two acids, glycocholic and taurocholic, cholestrin, mucus, and coloring matter. It is a ropy, viscid, and saponaceous liquid of a greenish-yellow color in man, greenish-brown in the ox, and emerald or grass-green in birds, reptiles, and fish. It has a bitter taste and an offensive odor. Its reaction is general alkaline; it is sometimes neutral but never acid, excepting in peculiar states of disease. It mixes in all proportions with water; it is not coagulated by heat. Alcohol renders it turbid by precipitating the mucns.

939. We have noticed (par. 921 and note page 304) that the two acids in the bile when treated with sulphuric acid and sugar acquire a purple color. Upon this reaction a test, called Pettenkofer's test, for bile has been founded. The best mode of applying the test for the detection of small quantities of bile in blood or other animal fluids is as follows: The alcoholic extract of the liquid to be tested for biliary matter is dissolved in a little water and mixed with a single drop of a solution of sugar (one part of sugar to four parts of water), and pure strong  $H_2SO_4$  is then added in small quantities till the turbidity at first produced disappears, cooling after each addition; it then for a few moments exhibits a yellowish color, which, however, soon changes to a pale cherry-red, then to deep carmine, then to purple, and finally to an intense violet tint. For the success of the experiment, care must be taken not to add too much sugar, otherwise a black mass will be formed which will completely mask the reaction. The temperature of the mixture must be allowed to rise to about  $50^{\circ} C.$ , but not higher. The reaction takes place with any kind of sugar and likewise with acetic acid.

#### A METHOD FOR ANALYZING QUALITATIVELY ANIMAL SECRETIONS.\*

940. The physical characters, such as color, taste, odor, consistence, etc., should first be carefully observed. The specific gravity may also be ascertained, when it can conveniently be done, as a knowledge of the density of the fluid will serve to furnish some indication of the amount of solid matter held in solution.

\* The method for analyzing the animal secretions, and for the analysis of urine, has been taken mainly from Gerhardt and Chancel's Qualitative Analysis.

941. The liquid should be examined by test-papers whether it is neutral, alkaline, or acid.

942. When the liquid holds in suspension any solid or semi-solid matter the dissolved should be separated from the undissolved portion either by decantation or by filtering it through paper or fine muslin. The microscopic examination of the residue generally furnishes some useful indications. The spontaneous coagulation in a secretion, at first limpid, is due almost always to fibrin.

943. The clear liquid is then submitted to the following examinations :—

944. *First examination.*—We heat a portion of the liquid in a test-tube; when the liquid is neutral or alkaline, one or two drops of acetic acid is first added to produce a *faint acid reaction*. If the liquid remains clear on warming it, we can be certain of the absence of albumen; in that case we pass on to the *second examination* (948).

945. If, on the contrary, the liquid becomes troubled or coagulated, it becomes necessary, after having agitated it, to divide it into two portions. To one portion add a few drops of dilute HCl; if the precipitate disappears it has not been due to albumen but was probably due to calcic or magnesian phosphate, or both. The other portion of the liquid must be examined by the microscope.

946. When the dilute HCl does not redissolve the precipitate, we then add a larger quantity of it and finally boil the mixture; if the precipitate becomes slowly dissolved and the liquid assumes a violet color (780), this reaction indicates the presence of *albumen*. We control this result by examining the action of nitric acid upon the primitive secretion (779 and 804).

947. If the coagulum formed by boiling the liquid, or the liquid itself, has a reddish tinge, *hæmatine* and also *globulin* may be present. In this case, we dry the coagulum; it then assumes a brown or black tint. It is afterwards boiled with alcohol to which a little  $H_2SO_4$  has been added; if it contains *hæmatine*, the liquid is colored red, and the alcoholic extract after having been evaporated to dryness furnishes a residue which gives, after calcination, the reactions of iron (935).

948. *Second examination.*—A liquid which does not contain albumen, or from which it has been separated by coagulation and filtration, may yet contain the following albuminoid substances, *casein*, *globulin*, *glutin*, *chondrin*, *pus*, and *mucus*, and possibly *paralbumin* and *metalbumin*.

949. A sample of the liquid is mixed with potassic ferrocyanide. If it remains clear, casein and globulin are absent (784), pass on to the third examination (par 951).

950. If a precipitate is formed, test for casein with solution of  $\text{CaCl}_2$ , and boil the mixture, which becomes turbid if casein is present (842). When this effect is manifested digest the liquid with rennet at a temperature of  $40^\circ \text{C}$ . in order to render the coagulation of the casein complete. If globulin is present the liquid will be rendered turbid by the addition of a few drops of acetic acid, and give afterwards a flaky precipitate when neutralized with  $\text{NH}_4\text{HO}$  (836).

951. *Third examination.*—To a portion of the liquid add acetic acid. If it remains clear, *pus*, *mucus*, and *chondrin* are absent; pass on to the fourth examination (par 953).

952. A precipitate is formed; test the solution with  $\text{HgCl}_2$ , if no precipitate is formed *pus* is absent. If the  $\text{HgCl}_2$  produces merely a turbidity, *mucus* or *chondrin* is, perhaps, present. Concentrate a portion of the liquid; the formation of a jelly indicates *chondrin* (860), the presence of which may be confirmed by its behavior with alum and metallic salts (864).

953. *Fourth examination.*—The liquid in which acetic acid produced no precipitate may yet contain gluten. Concentrate a portion strongly and leave it to cool; the formation of a jelly will indicate gluten, which may be further tested with  $\text{HgCl}_2$  (859).

954. *Fifth examination.*—The original liquid, or, if it contained albumen, the liquid freed from that compound by boiling, is concentrated by a gentle heat to a half or one-third of its volume, and is then left to cool; if no precipitate forms, the *urates* are probably absent. Pass on to the *sixth examination*.

955. If a precipitate is formed add acetic acid. If the *deposit previously amorphous* is seen (after the addition of the acid), under the microscope, to assume the form of rhombic tablets *uric acid* is indicated; confirm its presence by dissolving the deposit in  $\text{HNO}_3$  and examining it for uric acid as directed in par. 617.

956. *If the deposit is crystalline* and does not change its form by acetic acid, it points to the presence of *calcic sulphate* or *magnesian phosphate*; the presence of these salts must be confirmed by their reactions. The precipitate, if crystalline, may also contain *benzoic acid*, *calcic hippurate*, *tyrosine*, and *allantoin*.

957. *Sixth examination.*—The concentrated liquid in

which no precipitate is formed by boiling and subsequent cooling, or the liquid filtered from such a precipitate, is evaporated to a syrup on the water-bath and left to itself for a considerable time. If crystals gradually form, it is left to stand as long as they continue to increase. They may consist of *creatine*, *creatinine*, *glycocine*, *leucine*, *allantoin*, *taurine*, *sarcosine*, *inosite*, *alkaline hippurate*, *sodic chloride*, and *other inorganic salts*.

958. It must in the first place be determined whether these crystals are organic or inorganic. In the former case they must be tested especially for *nitrogen*, *sulphur*, and *phosphorus* (749, 750, 754), their chemical nature determined as nearly as possible, and the further examination regulated accordingly. If inorganic they must be examined according to the usual methods. If they blacken when strongly heated, but also leave a fixed residue, they probably consist of an organic acid, combined with an inorganic base; in that case the fixed residue will effervesce strongly with acids.

959. The syrupy residue itself, or the liquid, separated from the crystals which have formed in it, is evaporated nearly to dryness on the water-bath, and the residue is digested with alcohol of a sp. gr. of 0.83. The alcoholic solution and the substance insoluble in alcohol are separately examined.

960. *The alcoholic solution* is submitted to the following examinations:—

1. To a small portion of the alcohol solution concentrated and then diluted with water, is added, drop by drop, fuming nitric acid (containing nitrous vapors); if there is formed, after the addition, at the bottom of the liquid a zone at first green, next blue, violet, red, and lastly of a dirty yellow, it proves the presence of the *coloring matter of the bile* (933).

2. Another portion also concentrated and then diluted with water is mixed with sugar and  $H_2SO_4$ ; a beautiful purple red color proves the presence of the *acids in the bile* (939).

3. In a third portion we look for *glucose*. This substance generally communicates to the liquid a sweet taste. This portion of the alcoholic solution is evaporated to dryness on the water-bath, the residue is redissolved in water and examined for glucose by the copper test (880 and 881). The result ought to be controlled by the fermentation test (882).

4. The greater part of the alcoholic solution is evaporated to a very small volume, it is then mixed with *pure* nitric acid, which must be free *especially* from nitrous acid, and we place the vessel in a cooling mixture. If a crystalline deposit is formed, it is examined by the microscope to ascertain whether it has the appearance of nitrate of urea\* (895 to 897) or of hippuric acid or benzoic acid. The indications obtained by the microscope are confirmed by the chemical reactions.

5. A portion of the *concentrated* alcoholic solution is mixed with a syrupy solution of  $\text{ZnCl}_2$ ; if a precipitate is not formed even after a length of time, the liquid does not contain creatinine (898). If a precipitate is produced, we submit it to some special examinations, to ascertain the presence of creatine as well as creatinine (902).

6. Lastly, if the alcoholic solution possessed a strong acid reaction, it has still to be examined for lactic acid. To effect this the extract is concentrated and heated along with oxide or carbonate of zinc; a drop of the boiling filtered liquid is placed between two plates of glass, and we examine it by the microscope to see if the characteristic crystals of lactate of zinc are formed (908).

961. *Insoluble residue*.—In addition to *mucus* and undefined *extractive matters*, this residue can contain uric acid, a little casein, etc.

962. *Seventh Examination*.—After having finished the previous examinations, a portion of the *original* solution is evaporated to dryness on the water bath and the residue treated with ether. This dissolves the fatty matters, the presence of which we ascertain by evaporating the ethereal solution.

963. The portion insoluble in ether must be incinerated in a platinum crucible, and the inorganic salts determined by the ordinary methods.

#### QUALITATIVE ANALYSIS OF URINE.

964. The preceding method can, with some slight modifications, be applied to the analysis of most of the animal secretions.

965. Of the secretions, the urine presents a particular interest for the medical practitioner, owing to the changes

\* Care must be taken not to confound the alkaline nitrates for nitrate of urea.

which it undergoes in its composition by the effects of certain diseases, and which can be made use of as a means of diagnosis.

966. The bodies which normal urine holds in solution in water are:

<i>Organic Substances.</i>	<i>Mineral Substances.</i>
Urea.	Potassic
Uric acid.	Sodic
Hippuric acid.	Calcic
Creatine.	Magnestic
Creatinine.	Iron
Coloring and extractive matters.	Silicates.
Mucus of the bladder (in suspension).	Phosphates.
	Sulphates.
	Chlorides.

} Salts.

967. We find in addition, in normal urine, very small quantities of ammonia and of carbonic acid gas.

968. Recently emitted, it always possesses an acid reaction,\* due very probably to the presence of hippuric or uric acid. It behaves with reagents in the following manner:—

1. It is not coagulated by *boiling*.

2. The *caustic alkalis*, on being added to it, produce a turbidness, or a precipitate of the phosphates of the alkaline earths.

3.  $\text{BaCl}_2$  gives a precipitate of baric sulphate and phosphate.

4.  $\text{AgNO}_3$  gives a precipitate of argentic chloride and phosphate.

5. *Lead acetate* gives a precipitate of plumbic phosphate, sulphate and chloride.

6.  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  gives a precipitate of calcic oxalate.

7. *Alcohol* determines a turbidness which disappears by the addition of a sufficient quantity of water.

969. The following substances are only contained in the urine in certain diseases:—

1. Ammonic carbonate. Lactic acid. Albumen (in many diseases). Fibrine (found only in the sediments). Fatty substance (very rarely). Coloring matter of the bile (in

\* The experiments of Dr. Bence Jones show that when passed shortly after eating, the urine is often neutral, or even alkaline, becoming again gradually more and more acid up to the time when the next meal is taken.

liver complaints). Acids of the bile rarely. Glucose (diabetes). Sulphuretted hydrogen (very rarely). Calcic oxalate and cystine.

970. Before proceeding to the examination of the substances contained in the urine, it is necessary to observe the color, the transparency, the odor, the action upon test-paper. When the urine possesses an alkaline reaction, it is necessary to note if it is fresh, or if it is already commencing to undergo putrefaction.

971. It is equally useful to determine its density; the density of healthy human urine varies from 1.005 to 1.030.

972. After having obtained this preliminary information, we allow a quantity of the urine to stand for some time in order to allow time for the formation of a sediment. We then filter and examine separately the filtrate and the sediment.

973. *The filtrate.*—A quantity of the urine is boiled in order to coagulate the albumen\* when it is present, after that we examine the filtered liquid as described in par. 954. We at first look for the normal constituents of the urine, such as uric acid, the urates, hippuric acid, and urea; lastly those which are accidental, as ammonic carbonate, lactic acid, the coloring matter of the bile and glucose.

974. Ammonic carbonate can only be present in urine which has an alkaline reaction. The urine, which contains this ammonic salt, effervesces on the addition of an acid; when the urine is boiled with  $\text{KHO}$ ,  $\text{NH}_3$  is disengaged, and is recognized by its reactions (24).

975. Urine containing biliary matter is in general strongly colored; its tint varies from saffron yellow, to yellowish-brown; if the urine has a sediment, this is also colored. When we agitate a sample of this urine, there is formed on the surface a yellow scum.†

976. Urine containing sugar is usually characterized by its high specific gravity, which is frequently from 1.030 to 1.045, and occasionally as high as 1.050 and 1.055. If,

\* The precipitate produced by boiling is not a sure proof of albumen; since a white precipitate is also produced by boiling, when the urine (free from albumen) contains an excess of earthy phosphates; see pars. 945 and 946 for distinguishing the two precipitates.

† The taste of urine containing biliary matter is remarkably bitter, a peculiarity which furnishes a ready indication of its presence when other tests are not to hand; though it must not be implicitly relied on, since small traces may exist in the secretion without communicating to it any very decided taste (Bowman).

however, the sugar is present only in small quantity, the specific gravity may not be higher than usual; so that a moderately low specific gravity is of itself no proof of the absence of sugar. It is generally paler in color than normal urine; and it is generally slightly turbid.

977. Urine containing fatty or chylous matter is usually more or less turbid, and frequently has an almost milky appearance.

978. Urine containing sulphuretted hydrogen has the odor of rotten eggs; test for it as directed in par. 468.

979. *Sediments*.—The sediments ought to be examined microscopically as well as chemically.

980. The bodies contained in urinary sediments are—

Uric acid; the urates of lime, magnesia, potash, soda, and ammonia. Calcic oxalate. Calcic phosphate and magnesian ammoniac phosphate. Cystine. Different organic materials, such as mucus, blood, pus, spermatozoa, etc.

981. Free uric acid is only found in the sediments furnished by dark-colored urine, and it possesses a distinct acid reaction. These sediments are also colored; they can have a pale tint, but it is generally yellow, orange yellow, or brown; they have a granular appearance, and frequently even visibly crystalline to the naked eye. The uric acid can be very well detected with the microscope, or by its reaction with  $\text{HNO}_3$  and  $\text{NH}_4\text{HO}$  (617). It is distinguished from the urates by its insolubility in water, and by the fixed residue which these leave on incineration; it is distinguished from urate of ammonia by the latter disengaging ammonia in contact with  $\text{KHO}$ .

982. The urates also form a part of the sediments deposited from acid urine. The color of these sediments, as well as the urine, varies much. The urates contained in the sediments present frequently, to the naked eye, the appearance of mucus, of pus, and of blood, and can be distinguished only from these matters by microscopic observation and chemical analysis. Sodid urate is the one most frequently met with.

983. Calcic oxalate can make part of the sediment furnished by urine, the reaction of which is acid, neutral or alkaline, and it is not rare to find it associated with the urates. The urine containing calcic oxalate possesses a coloration, sometimes clearer, sometimes darker, than that of normal urine; its color is frequently that of amber yellow. Calcic oxalate, obtained by double decomposition, is an amorphous powder, whilst that found in the urinary



sediments is distinguished by its crystalline form. The identity of calcic oxalate is easily determined by the aid of its chemical reactions; when it is heated upon platinum foil, it is transformed into calcic carbonate without carbonization.

984. The phosphates of the alkaline earths are easily identified by the chemical reactions. (*See par. 198.*)

#### ANALYSIS OF CALCULI AND CONCRETIONS.

985. The number of substances which compose the calculi and concretions of animals is not considerable; the most frequent are:—

Uric acid and the urates.	Calcic oxalate.
Xanthine.	Calcic carbonate.
Cystine.	Magnesian carbonate.
Ammonic hippurate.	Cholesterin (with other
Calcic phosphate.	fatty matters).
Magnesian ammoniac phosphate.	Coloring matter of the bile.
	Fibrine.

986. The preceding substances are accompanied by the following bodies:—

The acids of the bile.	Extractive matters.
Albumen.	Soluble salts.
Mucus.	

987. The manner in which calculi comport themselves when calcined upon platinum foil by the aid of heat, permits of their division into many groups:—

#### CALCULI WHICH DO NOT LEAVE A FIXED RESIDUE.

988. *Calculi entirely combustible.*—They can be formed of uric acid, of ammoniac urate, ammoniac hippurate, of xanthine, of cystine, of cholesterin, of the coloring matter of the bile, of fibrine, or of albumen.

#### CALCULI WHICH LEAVE A FIXED RESIDUE.

A. *Calculi partially combustible.*—They can contain sodic urate, calcic urate, and all the organic matters quoted in combination with mineral substances.

B. *Calculi entirely fixed.*—They cannot contain any organic matter.

989. CALCULI WHICH DO NOT LEAVE A FIXED RESIDUE.—We treat a portion of this material with concentrated  $\text{HNO}_3$ , we evaporate to dryness, and we moisten the residue with a drop of ammonia.

990. It is colored purple-red (617):—

We pour upon the calculus a solution of $\text{KHO}$ , no disengagement of ammonia.	}	URIC ACID.
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In contact with the $\text{KHO}$ solution ammonia is disengaged.	}	AMMONIC URATE.
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991. It is not colored purple-red:—

The $\text{HNO}_3$ solution becomes <i>yellow</i> during the evaporation; the residue is insoluble in $\text{K}_2\text{CO}_3$ .	}	XANTHINE.
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The $\text{HNO}_3$ solution is colored dark brown by the evaporation; the residue dissolves in $\text{NH}_4\text{HO}$ , and deposits from this solution under the form of microscopic hexagonal tables.	}	CYSTINE.
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992. The calculus is heated upon platinum foil; it takes fire and burns with a very clear white flame; it cannot consist of cholesterin or of fibrine.

The calculus possesses evidently a crystalline texture, it dissolves in boiling alcohol, and is deposited as the solution cools under the form of shining spangles; it is insoluble in $\text{KHO}$ .	}	CHOLESTERIN.
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The calculus during the combustion develops the odor of burnt horn and becomes swollen; it dissolves in $\text{KHO}$ , from which acetic acid precipitates it; the precipitate dissolves in an excess of acetic acid, gives a solution which yields a precipitate with potassic ferrocyanide.	}	FIBRINE.
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993. The calculus possesses a brown color; it is friable, ochreous, and disengages the odor of calcined animal matter in burning.

It is little soluble in alcohol and water, it dissolves in $\text{KHO}$ which it colors dark brown; $\text{HNO}_3$ produces, in this solution, change of coloration characteristic of the coloring matter of the bile (983).	}	COLORING MATTER OF THE BILE.
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It is soluble in alcohol; the solution possesses a bitter taste; with $\text{H}_2\text{SO}_4$ and sugar it takes a beautiful reddish-violet color (989).	}	ACIDS OF THE BILE.
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994. CALCULI WHICH LEAVE A FIXED RESIDUE.—Two cases can present themselves:—

A. The matter does not give, with  $\text{HNO}_3$  and  $\text{NH}_4\text{HO}$ , the reaction of uric acid. (*See par. 617.*)

a. The residue from the calcination melts easily by heat.

<p>The calculus does not effervesce with acids either before or after the calcination; it dissolves in <math>\text{HCl}</math>, <math>\text{NH}_4\text{HO}</math> precipitates it from this solution; <math>(\text{NH}_4)_2\text{C}_2\text{O}_4</math> also precipitates it; heated with the blowpipe flame, moistened with a solution of cobaltic nitrate and again heated, it furnishes a blackish-brown enamel. (See par. 198.)</p>	}	<p>CALCIC PHOSPHATE.*</p>
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<p>During the calcination the calculus disengages an ammoniac odor; it dissolves without effervescence in acetic acid; <math>\text{NH}_4\text{HO}</math> forms in this solution a crystalline precipitate. Heated with the blowpipe flame along with a solution of cobaltic nitrate, it furnishes a dark-red glass. (See par. 198.)</p>	}	<p>MAGNESIC AMMONIC PHOSPHATE.</p>
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b. The residue from the calcination does not melt on being heated.

<p>The residue is white and does not turn red litmus blue; it gives the reactions of calcic phosphate (par. 188).</p>	}	<p>CALCIC PHOSPHATE.</p>
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<p>The original matter is not attacked by acetic acid; the mineral acids dissolve it without effervescence, and <math>\text{NH}_4\text{HO}</math> precipitates it from this solution; after calcination the residue possesses an alkaline reaction, and the acids then dissolve it with effervescence. (See par. 189.)</p>	}	<p>CALCIC OXALATE.</p>
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<p>When heated by the blowpipe flame the calculus becomes luminous; before calcination the acids dissolve it with effervescence; after the acid solution has been neutralized with <math>\text{NH}_4\text{HO}</math> it gives a white precipitate with ammoniac oxalate.</p>	}	<p>CALCIC CARBONATE.</p>
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B. The matter gives with  $\text{HNO}_3$  and  $\text{NH}_4\text{HO}$ , the reaction peculiar to uric acids. (See par. 617.)

a. It melts on being heated:—

<p>It communicates an intense yellow coloration to the flame.</p>	}	<p>SODIC URATE.</p>
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<p>It does not color the flame yellow, but violet. (See par. 46.)</p>	}	<p>POTASSIC URATE.</p>
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b. It does not melt on being heated:—

<p>The residue after calcination comports itself as calcic carbonate.</p>	}	<p>CALCIC URATE.</p>
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\* Calcic phosphate, although infusible itself, becomes fusible if mixed with magnesian ammoniac phosphate; the calculus produced by the mixture of these two phosphates is named, from its easy fusibility, the *fusible calculus*.

The residue after calcination dissolves with a slight effervescence in dilute $\text{H}_2\text{SO}_4$ ; the solution neutralized by $\text{NH}_4\text{HO}$ gives with sodic hydric phosphate a white precipitate.	}	MAGNESIC URATE.
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995. When the nature of the calculus has been determined, it is always necessary to control the results by special reactions.

#### VEGETABLE CHEMISTRY.

996. We have given the properties and reactions of the chief members in the three following groups: Albuminoid group; the saccharine or amylaceous group, and the group of the vegetable bases.

#### THE ALBUMINOID GROUP.

##### ALBUMEN, FIBRIN, CASEIN.

997. *Vegetable Albumen*.—This substance exists in the juice of most vegetables, and in the solid form in certain parts of the plant, especially in the seed. It exhibits the reactions, and appears to have the same composition, as animal albumen (794). “The mode of its occurrence differs, however, remarkably from that of animal albumen in this respect, that it is always found in plants in neutral or acid liquids, whereas animal albumen exists only in alkaline liquids.”

998. *Vegetable fibrine, gluten*.—This substance is also found in the juices of all nutritious vegetables. When the newly expressed juice is allowed to stand for a few minutes, the fibrine it contains separates in a coagulated state, more or less impure. The juice of grasses is especially rich in this constituent, but it is most abundant in the seeds of wheat and other corn plants. It may be obtained from wheat flour by a mechanical operation, and in a state of tolerable purity; it is then called gluten. It is a soft, glutinous, and elastic substance, which can be drawn out into long strings; it has scarcely any color, taste, or smell.

999. It exhibits the same reactions, and has the same composition, as animal fibrine (821).

1000. *Vegetable casein, legumine*.—This substance is found chiefly in the seeds of peas, beans, and similar leguminous seeds; hence it is frequently called *legumine*. Its composition has not been well determined, but Liebig

considers it to be identical with the caseine of milk, which it resembles in its reactions (828).

## THE SACCHARINE OR AMYLACEOUS GROUP.

1001. The substances forming this group are numerous; they contain, with a few exceptions, oxygen and hydrogen, in the *proportion* to form water. The sugars and gums are the only members of the group which are soluble in cold water; starch and other similar bodies are insoluble in cold, but soluble in hot water; whilst cellulose is quite insoluble in water, whether hot or cold.

1002. We may here observe that there are three leading varieties of sugar—CANE-SUGAR (*sucrose*), GRAPE-SUGAR (*glucose*), MILK-SUGAR (*lactose*), and some chemists add a fourth, fruit-sugar or fructose; other chemists consider it to be merely grape-sugar.

1003. We have restricted our notice of this group to the following members: CELLULOSE, STARCH, GUM, DEXTRINE, CANE- and GRAPE-SUGARS.

### CELLULOSE (*Lignin, woody fibre, C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>*).

1004. Cellulose forms the framework of all plants; its composition and reactions are always the same, but the properties which depend upon its state of aggregation present the greatest differences, as its texture varies with the plant from which it is extracted. Cotton, linen, hemp, and unsized white paper, consist of cellulose very nearly pure. "The easiest method of obtaining pure cellulose, is to wash white cotton, unsized paper, old linen, or elder-pith with a hot solution of KHO or NaHO, then with cold dilute HCl, then with NH<sub>4</sub>HO, washing thoroughly with water after the application of each of these reagents, and lastly, with alcohol and ether; it is often necessary to repeat this series of operations two or three times. To obtain pure cellulose from wood it is necessary, after boiling the wood with KHO till the liquid is almost dry, to treat it with chlorine water, or with a weak solution of chloride of lime, repeating these successive operations several times, in order to free the cellular tissue from the encrusting matter which is so intimately united with it.

1005. "Cellulose thus purified is white, translucent, of specific gravity about 1.5, insoluble in water, alcohol, ether,

and oils, both fixed and volatile. When quite pure it is unalterable in the air, but as it exists in wood, in contact with azotized and other easily alterable matters, it gradually decomposes in moist air, undergoing a slow combustion, and being converted into a yellow or brown friable substance called *touchwood*."

1006. *Dilute acids do not act on cellulose.*

1007. *Cold concentrated  $H_2SO_4$  disintegrates it and converts it into dextrine, a substance isomeric with cellulose, without blackening; if water be then added, and the liquid be subsequently boiled, the dextrine is converted into glucose.*

1008. By immersion in strong  $HNO_3$ , or in a mixture of  $HNO_3$  and  $H_2SO_4$ , or of  $KNO_3$  and  $H_2SO_4$ , cellulose is converted, without dissolving or undergoing any alteration of form, into a mixture of several explosive nitrogenous compounds, called gun-cotton, or pyroxylin. More dilute  $HNO_3$  converts it into substances allied to or identical with starch, gum, lactic acid, and malic acid; and if it is boiled with the acid for a length of time it is dissolved with complete decomposition.

1009. By immersion for a few seconds in  $HNO_3$  of ordinary strength hemp appears *pale yellow*, flax remains *unaltered in color*. New Zealand hemp (*Phormium tenax*) immediately becomes *blood-red*; the latter coloration is produced, even after bleaching, or after the fibre has been treated with a solution of KHO. This reaction may therefore serve for the detection of New Zealand hemp fibre in fabrics. The fibres of several plants are colored *pale-red* by the acid. The coloring is due to the incrusting substances. Cotton is scarcely or not at all colored by  $HNO_3$ , whereas animal fibres are colored permanently *yellow*. This reaction may serve for the detection of cotton in wollen textures.

1010. Unsized paper, if immersed for half a minute in a mixture of  $\frac{1}{4}$  to  $\frac{1}{2}$  volume of water and 1 volume of  $H_2SO_4$ , of ordinary strength, and immediately washed first with pure water, and then with water slightly ammoniacal, is changed into a substance called vegetable parchment. This substance can be formed from cotton as well as from flax fibres.

1011. The property of linen-fibre to acquire a deep yellow color by boiling with a mixture of equal quantities of water and KHO, whereas cotton is little or not at all colored by it, is applied by Böttger to the detection of linen in cotton.

1012. *Alkaline liquids* when dilute do not act upon cellu-

lose, but when concentrated they gradually destroy its texture.

1013. "Cellulose, in its natural state, is not colored blue by iodine; but after it has been digested for a short time with  $\text{H}_2\text{SO}_4$ , it becomes of a fine blue when free iodine is added. This reaction is sometimes serviceable in the microscopic examination of vegetable tissues; cellulose being thus easily distinguished from tissues into the composition of which nitrogen enters. By the prolonged action of  $\text{H}_2\text{SO}_4$ , the property of being colored blue by iodine disappears, the dextrine and sugar which are formed not being susceptible of the blue coloration."

1014. Cellulose dissolves completely in an ammoniac solution of  $\text{CuO}$ ,\* forming a syrupy liquid, which may be filtered after dilution with an equal bulk of water. It is precipitated from this solution in flakes on the addition of  $\text{HCl}$ .

#### STARCH (*Amylum*, *Fecula*, $\text{C}_6\text{H}_{10}\text{O}_5$ ).

1015. This substance is deposited in grains in the cellular tissue of certain parts of plants. The form and dimension of the starch grains are tolerably uniform in the same plant, but are very variable in different species of plants.

1016. It is insoluble in *alcohol*, *ether*, and *cold water*, but when a mixture of starch and water is heated to near the boiling point, the granules burst and disappear, forming a gelatinous mass. If this paste be largely diluted with water, the swollen granules of the starch subside, whilst a certain quantity of amylaceous matter remains in solution.

1017. When dry starch is heated to about  $205^\circ \text{C}$ ., it is converted into a substance isomeric with starch, called dextrine or British gum. This substance is soluble in cold water, forming a ropy solution much resembling gum in properties; but it differs from gum in forming a deep blue liquor in a solution of  $\text{CuSO}_4$ , which deposits  $\text{Cu}_2\text{O}$  when cold. It is rendered red and not blue with iodine. It has been called dextrine from its turning the plane of polarization to the *right*, when acting on polarized light.

1018. *Dilute alkalis and acids* in the cold cause starch to swell up and become partially disintegrated, but if the solution is heated it is converted into dextrine.

1019. An aqueous solution of iodine forms with starch a characteristic blue color; this color disappears if the

\* Prepared by dissolving  $\text{CuO}$  in ammonia.

iodine be added in excess, or if the solution be heated, but in the latter case, the blue color returns as the liquid cools. Decoloration of iodide of starch or its aqueous solution is produced by all reagents which cause the iodine to enter into combination, especially by chlorine, the color being restored by Zn and  $\text{H}_2\text{SO}_4$ ;  $\text{HNO}_3$  which converts iodine into iodic acid and destroys the starch;  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{AsO}_3$ ,  $\text{NH}_4\text{HO}$ , and  $\text{KHO}$ , the blue color when destroyed by the alkalies being restored by acids. Iodide of starch is likewise decolorized by  $\text{SbCl}_3$ ,  $\text{AsCl}_3$ ,  $\text{AuCl}_3$ , ferrons, manganoous, stannous, mercurous, mercuric and argentic salts. Slightly blued starch is decolorized by fixed oils. Alcohol and ether abstract part of the iodine from iodide of starch. Infusion of galls decolorizes iodide of starch; hence certain roots containing both starch and tannin are not rendered blue by iodine till after the addition of  $\text{HNO}_3$ . Decoloration is also produced by pyrogallie acid, by wood vinegar, by urine, and by tobacco vapor after the compound has been moistened with  $\text{H}\bar{\text{A}}$ . In presence of saliva, blood-serum, and other substances it is not produced until the liquid containing the starch has been mixed with 1–2 drops of tincture of iodine, then with a few drops of a solution of  $\text{KHO}$ , and lastly supersaturated with  $\text{HNO}_3$ .

#### GUM ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ).

1020. This substance is found in the juices of almost all plants, but is met with in its purest form in transparent tears, which exude from various species of acacia. Gum-arabic may be taken as its type.

1021. The gums proper are soluble in cold water or hot; but *mucilage* or *bassorin*, a modification of gum, is insoluble in water, but when moistened with it, swells up into a gelatinous mass. Gum-arabic dried at  $120^\circ$  becomes insoluble in water. The gum of seeds and roots or mucilage, which appears to be a universally diffused constituent of plants, is soluble in cold water, but is insoluble in alcohol and is precipitated from its aqueous solution by tincture of galls. Neutral lead acetate does not precipitate it completely, but the basic acetate produces complete precipitation.

1022. *Alcohol* and *ether* precipitate gum from its solution in water, in the form of white flocculi, or if dilute, in the form of a milky turbidity.



1023. Solution of KHO coagulates a solution of gum; but an excess of the reagent renders the liquid limpid.

1024. Concentrated  $\text{HNO}_3$  converts gum into mucic and oxalic acids.

1025. If it is boiled with dilute  $\text{H}_2\text{SO}_4$  it is transformed first into dextrin and then into glucose.

1026. If a few drops of  $\text{CuSO}_4$  be added to a solution of gum mixed with KHO, a blue precipitate is produced, which is insoluble in the liquid, but which is soluble in pure water, this solution can be boiled without depositing  $\text{Cu}_2\text{O}$ . This character distinguishes natural gum from dextrine (British gum) (1017).

### CANE-SUGAR OR *Sucrose* ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ).

1027. This variety of sugar is widely spread in the vegetable kingdom; it has been called cane-sugar because it is obtained chiefly from the sugar-cane. It has a specific gravity of 1.6. It is soluble in about one-third of its weight of cold, and is much more soluble in boiling water; its solution has, as is well known, a sweet taste. Absolute alcohol dissolves about 1-80th of this sugar at its boiling point, nearly the whole of which separates in small crystals on cooling. It is more soluble in ordinary alcohol. It slowly separates from a strong watery solution in large, transparent, colorless crystals, having the figure of a modified oblique rhombic prism; if a solution of it is kept at a temperature near the boiling point it gradually loses the property of crystallizing. It melts, about  $160^\circ \text{C}$ ., into a viscous colorless mass, which, on cooling, forms the solid known as barley sugar; if long kept this amorphous form cane-sugar gradually loses its transparency, and becomes crystallized. If, after the sugar has melted, the application of heat be continued, until the temperature reaches  $204^\circ$  or  $215^\circ \text{C}$ . the sugar loses an equivalent of water, and a brown, *deliquescent, slightly bitter and unfermentiscible substance* called *caramel* remains, which is used as a coloring matter by cooks and confectioners. If the heat is continued beyond  $215^\circ \text{C}$ ., complete decomposition ensues, inflammable gases are given off and a brilliant mass of porous charcoal remains.

1028. Cane-sugar is not rendered brown as grape-sugar is (879) on boiling it in a solution of KHO.

1029. "Concentrated  $\text{H}_2\text{SO}_4$  acts very energetically upon cane-sugar, evolving water, carbonic and formic acids and

charcoal. It is a striking experiment to mix about equal bulks of  $\text{H}_2\text{SO}_4$  and strong syrup; the mixture, when stirred, becomes brown and black, then suddenly heats, boils up, and passes into the state of a bulky black magma;\* the acid appears suddenly to abstract the elements of water from the sugar, leaving charcoal." The action of  $\text{H}_2\text{SO}_4$  upon grape-sugar is, as we have already noticed (877), very different.

1030. Strong  $\text{HNO}_3$  converts cane and grape-sugar into oxalic acid.

1031. When cane-sugar is boiled with dilute  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  it assimilates water and becomes converted into grape-sugar. Yeast effects the same change in its solutions. The converse change, that of converting grape-sugar into cane, has not yet been accomplished.

1032. A sugar solution has the property of dissolving many basic oxides, baryta and lime are very soluble in cold sugar solutions; when the solution of the alkaline earth is heated it becomes opaque, and when the solution reaches the boiling point the compound of sugar and the alkaline earth is deposited.

1033. If to a solution of cane-sugar a solution of caustic potash is added, and then a drop or two of a dilute solution of sulphate of copper, a deep blue liquid is obtained, which retains its *blue tint*, on being heated. This is a very good test for distinguishing the two varieties of sugar, or discovering an admixture of grape with cane-sugar. (See par. 880.)

1034. The properties of grape-sugar have already been described under animal chemistry, par. 876.

1035. Answers to the following exercises must be written out:—

#### EXERCISES.

180. State the method of examining a blood stain on linen, and the tests by which it is distinguished.

181. State the composition and principal properties of cellulose, describing particularly the action of strong  $\text{HNO}_3$  upon it.

182. How would you separate hippuric acid from human urine and exhibit its characteristic properties?

\* Cane sugar has been given as a test for free sulphuric acid in the presence of a sulphate. (See par. 407.)

183. Name the organic bodies usually present in urine, and give the methods for detecting them.

184. How would you distinguish ammoniac urate from magnesian ammoniac phosphate?

185. Give the composition of starch and the different kinds of sugar, and name some of their characteristic properties.

186. A deposit in urine is supposed to be uric acid. How would you ascertain whether such is the case?

187. How may urea be extracted from urine?

188. What are the tests for gelatine?

189. A deposit from urine is given you for chemical examination; what substances would you search for, and how would you conduct the examination?

190. What is the action of KHO on cupric salts, and how is this action modified in the presence of sugar?

191. What are the distinctive properties of the uric acid, xanthic acid, and cystic oxide calculi?

192. How would you analyze qualitatively a calculus composed of calcic phosphate and magnesian ammoniac phosphate?

193. How is a solution of gelatine obtained, and how does it differ from one of albumen?

194. Enumerate the different varieties of urinary calculi, and explain how they may be distinguished?

195. Why does urine become ammoniacal?

196. Describe the properties of albumen and fibrine.

197. Uric acid may exist as a urinary sediment in one or other of three states. What are these, and how may they be distinguished from each other?

## ORGANIC BASES AND MECONIC ACID.

1036. In this section the properties and reactions of the most important of the medicinal alkaloids and meconic acid, with reagents, are given, and the mode of extracting them in a state of purity from complicated mixtures of animal and vegetable substances; together with the more general methods of Stas and others, for the detection of poisonous alkaloids in organic mixtures.

## VOLATILE ALKALOID.

NICOTINA OR NICOTINE ( $C_{10}H_{14}N_2$ ).

1037. This alkaloid is contained in tobacco, probably in the state of malate and citrate; in its pure state it is a limpid, colorless, oily liquid; it absorbs oxygen on exposure to air, and turns brown and finally becomes solid. It has a strong and irritating odor of tobacco; is very inflammable, and burns with a smoky flame. It is miscible in all proportions with water, alcohol, and ether. It boils at  $250^{\circ}$  C., suffering, however, partial decomposition in the process; but when heated in a stream of hydrogen gas, it distils over unaltered, between  $100^{\circ}$  and  $200^{\circ}$  C. Its solutions possess an alkaline reaction. It precipitates metallic oxides from solutions of their salts, and unites with the acids, forming salts.

1038. Salts of nicotine are in general very soluble in water and alcohol, but insoluble in ether; they are difficultly crystallizable and even deliquescent.

1039. If an aqueous solution of nicotine, or a solution of a salt of nicotine mixed with a solution of NaHO or KHO, is shaken with *ether*, the nicotine is dissolved by the ether; if the latter is then allowed to evaporate on a watch-glass, the nicotine remains behind in drops and streaks; on warming the watch-glass, it volatilizes in white fumes of strong odor.

1040. *Chlorine-gas* acts powerfully upon nicotine, producing with it a blood-red liquid.

1041. Solution of I in KI and water, when added in small quantity to an aqueous solution of nicotine, produces a yellow precipitate, which after a time disappears. Upon a further addition of the iodine solution, a copious kermes-colored precipitate separates; but this also disappears again after a time.

1042. When a glass rod moistened with HCl is brought into contact with vapor of nicotine, white fumes are produced, as with ammonia. Boiled with HCl, the nicotine is colored violet.

1043. When  $HNO_3$  is heated with nicotine a red liquor is produced.

1044.  $PtCl_4$  produces in aqueous solutions of the chloride of nicotine a yellow crystalline precipitate of chloro-platinate of nicotine, which is insoluble in alcohol and ether,

slightly soluble in cold water, readily soluble in an excess of nicotine, and soluble in HCl in the cold.

1045.  $\text{AuCl}_3$  produces a reddish-yellow flocculent precipitate, sparingly soluble in HCl.

1046. "If an aqueous solution of nicotine is added to a solution of  $\text{HgCl}_2$  in excess, an abundant, flocculent, white precipitate is formed. If solution of  $\text{NH}_4\text{Cl}$  is now added to the mixture in sufficient quantity, the entire precipitate, or the greater part of it, redissolves. But the fluid very soon turns turbid, and deposits a heavy white precipitate.

1047. "Solution of *tannic acid* produces a copious white precipitate, which redissolves upon addition of HCl."

1048. Nicotine is extremely poisonous, a single drop of it being sufficient to kill a large dog.

1049. To extract nicotine from the animal tissues or the contents of the stomach, the animal matter is treated with a solution of KHO and then treated repeatedly with *ether* or pure *benzole*. The benzole or ether solution is evaporated at a gentle heat in a retort, the nicotine remains behind in an impure state. It is then treated with  $\text{H}_2\text{SO}_4$ , the solution, if necessary, filtered, and then treated with solution of KHO and ether or benzole as in the first instance. Nicotine may also be isolated from foreign organic matter by repeatedly exhausting the stomach, etc., with dilute acid, the acid solution is filtered and evaporated to dryness on the water bath; it is then redissolved in water and treated with KHO and ether in the manner previously described.

1050. The volatility and odor of nicotine are its most characteristic distinctions.

## NON-VOLATILE ALKALOIDS.

1051. The non-volatile alkaloids are solid, and cannot be distilled over with water.

### MORPHIA or MORPHINE ( $\text{C}_{17}\text{H}_{19}\text{NO}_3$ ).

1052. This alkaloid is contained in opium associated with narcotine and several other organic bases (see par. 1071). When crystallized from alcohol it forms small but very brilliant prismatic crystals, which are transparent and colorless; it crystallizes with an equivalent of water; at a gentle heat the water is expelled and the morphine

melts and forms a tumid resinous mass which solidifies into a radiated crystalline mass. When it is obtained by precipitation it appears as a white crystalline mass. It is soluble in about 1000 times its weight of cold and in 400 of boiling water; the solution has a bitter taste. It is soluble in about 90 times its weight of cold, and from 20 to 30 parts of boiling alcohol. Its aqueous and alcoholic solutions manifest distinctly alkaline reactions. It dissolves in amyl-alcohol in the cold but more freely with the aid of heat; it is soluble in acetic ether. It dissolves according to Schlimper in 60 parts and according to Pettenkofer in 175 parts of chloroform. Its solubility in ether varies according to its physical condition, recently precipitated morphia dissolves in ether about three times as largely as the crystallized base; therefore, if a solution of a morphine salt has been neutralized with one of the fixed alkaline carbonates or acid carbonates ether dissolves the precipitated morphine if the ether is shaken up with the liquid at once, but not after some time, or at least to a very slight extent, as the precipitated base in time becomes crystalline, and in that condition is nearly insoluble in ether. Ether containing alcohol dissolves morphine.

1053. Acids dissolve morphine, forming with it salts which are most of them crystallizable. They are readily soluble in water and alcohol, but insoluble in ether. Its salts are exceedingly bitter to the taste.

1054. The fixed alkalies and ammonia precipitate morphine from the solution of its salts, an excess of the precipitant redissolves the precipitate. The precipitated morphine redissolves with great readiness in the fixed alkalies, but much less readily in ammonia. Lime-water behaves like the fixed alkalies.

1055. The fixed alkaline carbonates precipitate morphine from the solution of its salts, and it does not redissolve in an excess of the precipitant. The fixed alkaline acid carbonates also precipitate it, and an excess does not redissolve the precipitate; these reagents fail to precipitate morphine from acid solutions in the cold.

1056. Precipitated morphine dissolves in  $\text{NH}_4\text{Cl}$ , and with difficulty in  $(\text{NH}_4)_2\text{CO}_3$ .

1057. If a neutral and concentrated solution of a ferric salt be added to neutral and concentrated solutions of salts of morphine, a beautiful dark blue color is produced, which is characteristic of morphine. The color is not permanent, and it is destroyed by an excess of acid, by the

action of heat, and even by the addition of alcohol. If the solution contains an admixture of animal or vegetable extractive matters or of acetates, the color will appear clouded or less distinct.

1058. Concentrated  $\text{HNO}_3$  colors morphine or its salts in the solid state, and also their *concentrated* solutions orange red, which passes by degrees to yellow; this coloration is not peculiar to morphine.

1059. Iodic acid is reduced by morphine either free or combined, the liquid turning brown and emitting an odor of iodine. When solid morphine or a morphine salt is moistened with a solution of 1 part of iodic acid in 15 parts of water, and a solution of 1 part of starch in 400 parts of water is added, a *blue color* is produced, by which  $\frac{1}{3000}$ th of a grain may be detected: if a drop of the starch solution be previously evaporated with the morphine, the reaction will suffice for the detection of  $\frac{1}{100000}$ th of a grain. If a layer of very dilute ammonia be poured upon a solution of morphine mixed with iodic acid and starch, then, even if only  $\frac{1}{200000}$ th of morphine is present, two colored rings will be formed at the surface of contact, the upper being blue, the lower brown; in more dilute solutions only the brown ring is produced. Other substances capable of reducing iodic acid may likewise produce the blue ring, but not the brown ring at the same time (A. Duprè).

1060. Dissolve morphine in strong  $\text{H}_2\text{SO}_4$  in the proportion of 0.002 to 0.004 grain to 6 or 8 drops of the acid, then add a drop of  $\text{HNO}_3$ ; whereupon, if the morphine solution has been recently prepared, a *rose-color* is produced, changing after a few seconds to *yellow*, then to *greenish*, and finally to brown. If a small quantity of water be added to the solution of morphine in  $\text{H}_2\text{SO}_4$ , so that the mixture becomes hot, the coloring produced by the subsequent addition of  $\text{HNO}_3$  is of a much deeper carmine red, and much more durable. If the sulphuric solution is heated for a few minutes to  $100^\circ$ – $150^\circ$ , the addition of a drop of nitric acid produces, after cooling, a splendid deep violet color, which gradually disappears from the centre outwards, passing through blood-red. If the temperature is raised above  $150^\circ$  the liquid acquires of itself, at a certain moment, a violet-rose color; at still higher temperatures, a dirty green color is produced. On adding a drop of  $\text{HNO}_3$ , after cooling, the liquid immediately turns red, without passing through violet. A solution of morphine in  $\text{H}_2\text{SO}_4$ , left to itself for twelve to

twenty-four hours at ordinary temperatures, behaves as if it had been heated to  $100^{\circ}$ – $150^{\circ}$ ; as regards the sensibility of these reactions  $\frac{1}{6}$  of a milligramme of morphine is sufficient to produce a very bright carmine color;  $\frac{1}{80}$  of a milligramme gives a very distinct reaction, and  $\frac{1}{100}$  milligramme still gives a perceptible tint after half a minute.—*Husemann.*

1061. A solution of morphine in  $\text{H}_2\text{SO}_4$ , previously heated, is colored deep red by ferric chloride, the color changing after a time to dirty green.

1062. To detect morphine when mixed with animal matter, the substance is mixed with alumina, dried between  $100^{\circ}$  and  $110^{\circ}$ , then well pulverized and macerated in cold water acidulated with acetic acid. The solution treated with ammonia deposits morphine, which may then be recognized by its reactions with iodic acid, ferric salts,  $\text{H}_2\text{SO}_4$ , and  $\text{HNO}_3$ .

#### NARCOTINA OR NARCOTINE ( $\text{C}_{22}\text{H}_{23}\text{NO}_7$ ).

1063. Narcotine appears in the form of acicular groups, or in colorless, brilliant, right rhombic prisms, or when precipitated by the alkalis, as a white, loose, crystalline powder. It fuses at  $171^{\circ}$  C., solidifies again at  $130^{\circ}$  C. in the crystalline or amorphous state, according as the cooling is slow or rapid. It is insoluble in cold water, but dissolves in boiling water to the extent of 1 part in 7000. It dissolves sparingly in alcohol and ether in the cold, but somewhat more readily upon heating. Solid narcotine is tasteless, but the alcoholic and ethereal solutions are intensely bitter. It dissolves in 2.6 parts of chloroform, in 60 parts of acetic ether, also in oils, both fixed and volatile. Its solutions do not possess an alkaline reaction.

1064. Narcotine dissolves readily in acids, forming with them salts, but the basic powers of narcotine are so feeble that its salts have invariably an acid reaction. "Those with weak acids are decomposed by a large amount of water, and, if the acid is volatile, even by simple evaporation. Most of the narcotine salts are amorphous, and soluble in water, alcohol, and ether; they have a bitter taste."

1065. The alkalis, and the carbonates and acid carbonates of the alkalis, precipitate narcotine immediately from a solution of its salts, in the form of a white powder, which,



seen through a lens magnifying 100 times, appears an aggregate of small crystalline needles; the precipitate is insoluble in an excess of the precipitant. If a solution of narcotine is mixed with ammonia, and ether added in sufficient quantity, the narcotine which has separated upon the addition of the ammonia redissolves in the ether, and the clear fluid presents two distinct layers. If a drop of the ethereal solution is evaporated on a watch-glass, the residue is seen, upon inspection through a lens magnifying a hundred times, to consist of small, distinct, elongated, and lance-shaped crystals.

1066. "*Concentrated*  $\text{HNO}_3$  dissolves narcotine to a colorless fluid, which acquires a pure yellow tint upon the application of heat.

1067. "If the solution of a salt of narcotine is mixed with *chlorine-water*, it acquires a yellow color, slightly inclining to green; if ammonia is then added, a much more intensely colored yellowish-red fluid is obtained.

1068. "Narcotine added to cold  $\text{H}_2\text{SO}_4$  colors it bluish-violet or yellow, which, if the liquid be gently heated, changes to orange-red, then to violet-blue at the edge of the dish, and lastly violet-red. This reaction is very distinct, if the  $\text{H}_2\text{SO}_4$  contains 1 part in 2000 of narcotine; and even if it contains only 1 part in 40,000 a slight carmine color is still perceptible, passing into violet-red."—*Husemann*.

1069. A solution of narcotine in cold  $\text{H}_2\text{SO}_4$  becomes reddish-yellow on addition of  $\text{HNO}_3$ ; with hypochlorite of soda the same color is produced, but preceded by a carmine tint. If the solution has been heated, both reagents immediately produce a light yellow color, becoming slightly reddish after a while.

1070. A solution of narcotine in  $\text{H}_2\text{SO}_4$ , previously heated, acquires, on addition of ferric chloride, a dark red color, changing into cherry-red, which lasts twenty-four hours.

1071. Opium contains, besides morphine and narcotine, the following crystallizable alkaloids—*codeine*, *thebaine*, *narceine*, and *papaverine*. The following table shows the difference in the solubility of these alkalies in different liquids:—

	Water.	Alcohol.	Ether.	Potash.
Morphine .	Slightly soluble	Easily soluble	Almost insoluble	Soluble in an excess.
Narcotine . .	Almost insoluble	Soluble	Soluble	Insoluble.
Narceine . .	Slightly soluble	Soluble	Insoluble	Soluble in weak potash.
Codeine . . .	Soluble	Extremely soluble	Extremely soluble	Insoluble in concentrated potash.
Thebaine . .	Insoluble	Soluble	Soluble	Soluble in weak potash.
Papaverine .	Insoluble	Soluble	Soluble	Insoluble.

### QUINA OR QUININE ( $C_{20}H_{24}N_2O_2$ ).

1072. This alkaloid exists in combination with kinic acid in cinchona barks; it forms two hydrates, containing respectively 1 and 3 atoms of water; the latter is the ordinary hydrate. It appears either in the form of silky needles, or as a loose white powder. It melts at  $120^{\circ} C.$ , and gives up its water of crystallization. It requires about 350 parts of cold water and 200 of boiling water for its solution. It is readily soluble in alcohol, both hot and cold; it is less soluble in ether; it dissolves in 60 parts of the latter liquid. It is also soluble in chloroform and the essential and fixed oils. Its solutions have an alkaline reaction and are intensely bitter.

1073. Acids dissolve quinine, forming with it salts which are crystallizable, and difficultly soluble in cold, but readily soluble in hot water and in spirit of wine. The acid salts dissolve very freely in water; the solutions exhibit the remarkable phenomenon of *fluorescence* or *epipolic dispersion*—a magnificent blue luminosity seen upon the surface of the liquid when viewed in reflected light, and which is owing to a change effected in the *actinic* rays by the dissolved quinine salt. The salts of this base are intensely bitter.

1074. The fixed alkalies, ammonia, and the alkaline carbonates precipitate quinine as trihydrate from a solution of its salts in an amorphous state, which after some time becomes crystalline. The precipitate is only soluble in the fixed alkalies to a barely perceptible extent; but it is more soluble in ammonia. In the solutions of the fixed alkaline carbonates, it dissolves to about the same extent as in pure water.

1075. "The addition of *chlorine-water* to the solution of a salt of quinine fails to impart a color to the fluid, or at

least imparts to it only a very faint tint; but if ammonia is now added, the fluid acquires an intense emerald-green color; by this reaction, especially by employing an ethereal solution, mere traces of quinine may be recognized; quinine, however, exhibits the same reaction. If, after the addition of the chlorine water, some solution of potassic *ferrocyanide* is added, then a few drops of ammonia or some other alkali, the fluid acquires a magnificent deep red tint, which, however, speedily changes to a dirty brown. This reaction is delicate and characteristic. Upon addition of an acid (acetic acid answers the purpose best) to the red fluid, the color vanishes, but reappears afterwards upon cautious addition of ammonia.

1076. As cinchonine and quinidine exist together with quinine in cinchona-barks, their sulphates may occur as impurities in sulphate of quinine; they may be recognized by the following *quinine test* of Liebig: 10 grains of the sulphate to be tested are warmed with 10 drops of dilute  $\text{H}_2\text{SO}_4$ , and 15 drops of water in a test tube, the solution is allowed to cool, and then 60 drops of commercial ether and 20 drops of ammonia-water are added, and the whole is shaken and the tube stopped. If the quinine were free from cinchonine, and did not contain more than 10 per cent. of quinidine, the whole remains in solution; but if cinchonine were present, it is deposited as a white pulverulent layer between the ether and the water, as is also the case with quinidine when present in large quantity. Smaller portions of quinidine crystallize from the ether on standing for a short time, and still smaller quantities when ether saturated with quinidine is employed in the first instance. As it sometimes happens that the upper ethereal layer solidifies to a jelly, even with pure sulphate of quinine, it is more convenient to employ ether containing alcohol, or to take a somewhat larger proportion of ether than is directed above.—*Gmelin*.

1077. Stoddart has proposed the following modification of Liebig's process: Into a glass tube or bottle put 10 grains of the suspected salt, dissolve in 10 minims of dilute  $\text{H}_2\text{SO}_4$  and 60 minims of distilled water; to this add 150 minims of pure ether, 3 minims of alcohol, and 40 minims of a solution of soda (1 part of solid  $\text{NaHO}$  to 12 of water). Agitate well and set aside for twelve hours, when, if the slightest trace of quinidine or cinchonine be present, they will be seen at the line of separation between the ether and solution of  $\text{Na}_2\text{SO}_4$ . If only a small percentage of quini-

dine be present, it will appear as an oily substratum appearing under a lens as dust, from the minuteness of its particles. Cinchonine will appear more decidedly crystalline. With a little practice the eye will easily distinguish which of the alkaloids is deposited.

#### CINCHONINE ( $C_{20}H_{24}N_2O$ ).

1078. This alkaloid exists together with quinine, in most of the true cinchona barks; it appears either in the form of transparent brilliant, four-sided prisms, or fine, white, crystalline needles, or, if precipitated from concentrated solutions, as a loose white powder; in its crystalline state it is anhydrous. It is nearly insoluble in cold water, and requires for solution 2500 parts of boiling water. It is less soluble in alcohol than quinine and is more soluble in hot than cold alcohol. The greater portion of the cinchonine dissolved by hot alcohol, separates in a crystalline form as the solution cools. It dissolves in 470 parts of boiling ether and 23.2 parts of chloroform. Solutions of cinchonine have an alkaline reaction and a bitter taste. It fuses at  $165^{\circ} C.$ , to a colorless liquid which becomes a crystalline mass on cooling.

1079. The acids dissolve cinchonine, forming with it salts which are most of them crystallizable; they are soluble in water and alcohol, insoluble in ether. They are exceedingly bitter to the taste.

1080. The fixed alkalies, ammonia, and the neutral alkaline carbonates precipitate cinchonine from a solution of its salts, in an amorphous state, an excess of the precipitant does not redissolve the precipitate.

1081. "If the solution of a salt of cinchonine containing only very little or no free acid, is mixed with potassic ferrocyanide, a flocculent precipitate of ferrocyanide of cinchonine is formed. If an excess of the precipitant is added, and a gentle heat very slowly applied, the precipitate dissolves, but separates again upon cooling, in brilliant gold-yellow scales, or in long needles, often aggregated in the shape of a fan. With the aid of the microscope, this reaction is as delicate as it is characteristic."

#### STRYCHNINE ( $C_{21}H_{23}N_3O_2$ ).

1082. This alkaloid exists, together with brucine and igasurine, in *nux vomica*, in *St. Ignatius' beans*, in the *strychnos colubrina*, and several other varieties of *strych-*

nos; it crystallizes from dilute alcohol, in white anhydrous octohedra, or in square prisms, which do not fuse on the application of heat; when it is produced by precipitation or rapid evaporation, it appears as a white powder. Cold water does not dissolve more of it than  $\frac{1}{7000}$ th of its weight, and it is only slightly more soluble in hot water. It is only sparingly soluble in dilute alcohol, and almost insoluble in absolute alcohol and ether. It dissolves freely in amyl-alcohol, and is soluble in chloroform and the essential oils. It is very bitter to the taste; even when its cold aqueous solution is diluted with 100 times its weight of water, it still possesses a distinctly bitter taste.

1083. Acids dissolve strychnine, forming with it salts, most of which are crystallizable; they are soluble in water, and are very bitter to the taste.

1084. The fixed alkalies and their carbonates precipitate strychnine from solutions of its salts. The precipitate is insoluble in an excess of these reagents; and the strychnine is only precipitated after the lapse of some time from dilute solutions.

1085. Ammonia precipitates strychnine from a solution of its salts, but the precipitate is soluble in an excess of the ammonia, from which solution the strychnine separates after some time, in the form of needles; the length of time required for the separation depending upon the strength of the solution.

1086. If strychnine is dissolved in a drop or two of *pure* concentrated  $H_2SO_4$  (the acid must be free from nitrous acid), it forms a colorless solution, which yields colored reactions with most oxidizing substances; the oxidizing substances are added in the solid form, and in small quantities. The following reagents give the colorations named, with the sulphuric solution of strychnine: *a. Peroxide of lead* gives a blue coloration, becoming violet, then red, and finally, in a few hours, yellow. *b. Acid potassic chromate* gives a fine violet coloration; if the quantity of strychnine present is large, the color is pale blue. *c. Potassic ferrocyanide* yields a somewhat similar reaction to *b*, but more permanent. *d. Black oxide of manganese* affords a violet coloration, becoming dark red in the course of an hour. The presence of *santonin*, or *starch*, does not prevent the recognition of strychnine by acid potassic chromate in the above solution; *sugar*, *quinine*, or *morphine* renders it indistinct, but does not affect the reaction with peroxide of lead. The presence of thirty

parts of tartar emetic does not prevent the coloration with acid potassic chromate, but sixty parts render it indistinct. Very small quantities of animal or vegetable extractive matters render the above reactions indistinct, where the strychnine is present in minute traces only. It is, therefore, always advisable to free the strychnine first, as far as practicable, from all foreign matters before proceeding to try any of these color tests; methods for freeing it from organic matter are given in pars. 1089, 1090, and 1091. *These, and similar color experiments, ought to be performed on a piece of white porcelain.*

1087. Concentrated  $\text{HNO}_3$  dissolves strychnine, forming a solution colorless in the cold, but which becomes slightly yellow on heating if the strychnine is pure.\* If to this solution a small quantity of peroxide of lead be added, the same changes of color may be witnessed as in the preceding experiment.

1088. "Strychnine is associated in nature with the next base, brucine, which may be readily distinguished from it by being soluble in absolute alcohol. The action, too, of nitric acid upon the two bodies differs; it dissolves brucine and colors the solution intensely red; when heated, this color changes to yellow; and if  $\text{SnCl}_2$  or  $(\text{NH}_4)_2\text{S}$  be then added, the color again changes and becomes a most intense violet."

1089. *Detection of Strychnine in the presence of Animal Matter.*—The mixture to be examined, which, if solid, should be cut into small pieces, must be digested in dilute  $\text{HCl}$  (one part of strong acid with ten parts of water) at a temperature of  $60^\circ$  to  $80^\circ \text{C}$ . The liquid is strained and the residue is again exhausted with hot water containing  $\text{HCl}$ . The extracts are then mixed with a slight excess of ammonia, and evaporated to dryness on the water-bath, together with some clean sand. The dry residue is exhausted three or four times with hot amyl-alcohol, and these alcoholic solutions are filtered through paper moistened with the alcohol. The filtrate contains, besides strychnine, fat and coloring matter, which are got rid of by shaking the filtrate with ten or twelve times its volume of hot water containing  $\text{HCl}$ ; the strychnine is dissolved in the acidulated water, whilst the greater part of the fat

\* If brucine is present in the strychnine, which is the case with most commercial specimens, the color produced by the  $\text{HNO}_3$  is deep orange or red. (See par. 1088.)

and coloring matter remains in the amylic alcohol. The hot acid solution must be shaken with fresh portions of the alcohol, so long as the alcohol continues to dissolve fat and coloring matter; after this the acid solution, mixed with a slight excess of ammonia, is evaporated on the water-bath, and the residue again exhausted with hot amylic alcohol, which dissolves the free strychnine and leaves it behind on evaporation. If the strychnine should not be sufficiently pure, it is again dissolved in dilute HCl, shaken with amylic alcohol, and the process continued as before. When pure, it may be recognized as directed at par. 1086.

1090. "The presence of strychnine may be detected in very minute quantities in complicated *organic liquids*, by rendering them alkaline with a solution of KHO, and agitating thoroughly with a few drachms of chloroform; the chloroform dissolves the strychnine, and leaves it in the solid form on evaporation. From this residue it may be extracted by dilute HCl, and may afterwards be submitted to the usual tests."

1091. To detect strychnine in *beer*, shake the beer with animal charcoal in the proportion of four ounces of charcoal to a gallon; let it stand over night, collect and wash the charcoal once or twice with cold water, and boil it for half an hour with eight ounces of alcohol, which takes up the strychnine. The residue which remains on evaporating the alcohol is shaken with a few drops of KHO and ether, the latter of which takes up the strychnine. The alkaloid may be recognized after evaporating the ethereal solution, by means of  $H_2SO_4$  and acid chromate of potash.—*Graham and Hofmann*.

#### BRUCINE ( $C_{23}H_{26}N_2O_4$ ).

1092. In addition to the sources of this alkaloid named in par. 1082, it exists in large quantity, unaccompanied by strychnine, in false angustura bark. It appears either in the form of transparent oblique rhombic prisms, or in that of crystalline needles. It melts readily on the application of heat, and loses its water of crystallization. It is easily distinguished from strychnine, which it resembles in many respects, by its ready solubility, both in dilute and absolute alcohol. It is difficultly soluble in cold, but somewhat more soluble in hot water; one part dissolving in about 850 parts of cold and 500 parts of boiling water. It is

soluble in amyl-alcohol. It is insoluble in ether and fixed oils. Its taste is intensely bitter.

1093. The acids dissolve brucine, forming salts, most of which are crystallizable; they are readily soluble in water and are very bitter to the taste.

1094. The fixed alkalies and their carbonates precipitate brucine from a solution of its salts; the precipitate is not soluble in an excess of these reagents. "Viewed under the microscope immediately after precipitation it appears to consist of very minute grains; but upon further inspection these grains are seen—with absorption of water—to suddenly form into needles, which latter subsequently arrange themselves, without exception, into concentric groups. These successive changes of the precipitate may be traced distinctly even with the naked eye."

1095. Ammonia precipitates brucine from its solutions; the precipitate appears at first in the form of minute drops of oil, but which finally change to white needles. The precipitate is very soluble in an excess of ammonia; but it is deposited after a time, the length of time depending upon the strength of the solution, from the ammoniacal solution in a crystalline state.

1096. The nitric acid reaction described in par. 1088 is characteristic for brucine.

### MECONIC ACID ( $C_7H_5O_7H_3$ ).

1097. This acid is one of the constituents of opium; it crystallizes in micaceous scales, or small rhombic prisms, containing 3 atoms of water, which it gives off at  $100^\circ C.$ , leaving a white, opaque, effloresced mass. It has a sour taste, and reddens litmus strongly. It dissolves readily in water and alcohol, less easily in ether.

1098. It is easily oxidized by  $HNO_3$ , and it is also decomposed on being boiled in a strong solution of  $KHO$ .

1099. Ferric chloride imparts to solutions of the acid and its salts a blood-red color, which is distinguished from ferric acetate by not altering in color by boiling, and from ferric sulphocyanide by not being bleached by treatment with corrosive sublimate.

1100. Plumbic acetate precipitates the acid from its solutions as plumbic meconate; this lead salt is decomposed by  $H_2S$ ,  $PbS$  being formed, and meconic acid set free.



*Detection of opium in organic mixtures, tissues, etc.*

1101. If the suspected substance is a solid it should be cut into small pieces; if it is *not in the solid state* it should be evaporated nearly to dryness on the water-bath. The original solid, or the solid obtained by evaporation, must be digested in a small quantity of water containing a little acetic acid either in a flask or dish on the water-bath for an hour or so; the mixture is then filtered, and to the filtrate, which must still contain a slight excess of acetic acid, is to be added plumbic acetate as long as any precipitate is produced; the meconic acid, if present, will be precipitated (par. 1100), whilst the morphia will remain in solution in combination with acetic acid. The mixture must be warmed, but not boiled, and afterwards allowed to cool. When cold it is filtered, the filtrate is examined according to 1103, and the precipitate according to 1102.

1102. The precipitate, having been thoroughly washed with water, is removed into a beaker and mixed with water; a current of  $H_2S$  is then passed through the mixture, which is occasionally stirred during the passage of the gas; when the gas is in excess the mixture is filtered; the filtrate contains the meconic acid, the precipitate consisting of  $PbS$ . The filtrate is warmed and, if necessary, concentrated at a temperature not exceeding  $71^\circ C.$ , to expel the  $H_2S$ . It is then tested for meconic acid as directed at par. 1099.

1103. To the filtrate from the acetate of lead precipitate, and which will contain the morphia if present, is added  $H_2S$  in excess to precipitate the excess of  $Pb$  which was added; when the gas is in excess the mixture is filtered, and the filtrate which contains the morphia as acetate is evaporated to a small bulk on the water-bath. To the concentrated solution is added potassic carbonate slightly in excess, which precipitates the morphine; the mixture is then agitated with an ethereal solution of acetic ether. After subsidence the ethereal solution is poured off and allowed to evaporate spontaneously, when there is left a residue of morphia in more or less well-defined crystals, to which the tests 1059, 1060, can be successfully applied.

*Methods for the detection of poisonous alkaloids in organic mixtures.*

1104. When the organic bases have to be sought for among the *contents* of the stomach or intestines, or in *arti-*

cles of food, or in pappy matters, the substances to be examined are treated with twice their weight of pure absolute alcohol, to which from ten to thirty grains of tartaric or oxalic acid, in preference tartaric acid, have been added, and the mixture is heated in a flask or retort to between  $70^{\circ}$  and  $75^{\circ}$  C. When quite cold the mixture is filtered and the insoluble portion is washed with strong alcohol, the washings being collected with the filtrate. The filtered liquid is evaporated in vacuo, or in a tubulated retort, through which a strong current of air is passed at a temperature of not more than  $33^{\circ}$  C. If, after the volatilization of the alcohol, the liquid residue contains fatty or other insoluble matters, it must be again filtered, the filter being moistened with water, and the filtrate and the washings of the residue on the filter evaporated under an air-pump or under a bell-jar over concentrated  $\text{H}_2\text{SO}_4$  until nearly dry. The residue is then treated with cold absolute alcohol, taking care to exhaust the substance thoroughly; this alcohol solution is left to evaporate in the open air at the ordinary temperature, or still better in vacuo; this residue we will name *a*.

1105. *Solid matter*, such as the lungs, liver, heart, etc., must be cut into very small pieces, then moistened with absolute alcohol acidified with tartaric or oxalic acid as in the preceding par.; after pressing out the liquid this treatment with alcohol must be repeated *until all the soluble matter is completely extracted*. Collect the fluids obtained, and filter and allow the filtrate to evaporate in the open air at the ordinary temperature, or better still in vacuo; this residue we will name *b*.

1106. The *a* or *b* residue must be dissolved in the smallest possible quantity of water, and pure acid carbonate of soda or potash *in powder* must be added gradually to the solution until it is neutralized. The neutralized solution must be *immediately* shaken with four or five times its volume of *pure* ether to dissolve the alkaloid; it must be allowed to settle, and when the layer of ether has become perfectly clear, a little of it is removed into a watch-glass, and allowed to evaporate spontaneously. If after the evaporation of the ether oily streaks remain upon the glass and gradually collect together at the bottom of it, a *liquid and volatile* alkaloid is probably present. If this be the case, the warmth of the hand will be sufficient to cause the contents of the watch-glass to exhale a disagreeable smell, which, according to the nature of the alka-

loid, is more or less sharp, choking, and irritating. *When a volatile alkaloid is indicated*, examine the ether solution according to par. 1109.

1107. If the residue left in the watch-glass on the evaporation of the ether is a *solid*, or *turbid fluid* with *solid particles* suspended in it, a *solid non-volatile alkaloid* is indicated; in this case the warmth of the hand may cause the residue to emit a disagreeable animal smell, but not a pungent odor. When a non-volatile alkaloid is indicated examine the ether solution according to par. 1111.

1108. Stass's process is given for the purification when a volatile alkaloid has been indicated, and Otto's modification of Stass's method when a non-volatile alkaloid is suspected.

1109. *A volatile alkaloid has been indicated in the trial sample.* To the solution from which the trial sample of ether was taken, add one or two cubic centimetres of a strong solution of KHO or NaHO; shake the mixture, then let it rest until the ether solution has separated perfectly from the alkaline one; then remove the ethereal (supernatant) fluid into a flask, and treat the alkaline solution with a fresh portion of ether as before; draw off the ether solution into the flask which contains the former ether fluid, and repeat the treatment of the alkaline fluid with ether two or three times more, the ether solutions so obtained being all mixed together; the mixture is then to be shaken with 1 or 2 cubic centimetres of a mixture of 4 parts by weight of water and 1 part by weight of  $\text{H}_2\text{SO}_4$ ; after being allowed to stand, the ether is drawn off, and the acid liquid is washed with a second quantity of ether. As the sulphates of the volatile alkaloids are soluble in water, and as almost all of them are insoluble in ether, the alkaloid sought is contained in the acid solution in the form of pure sulphate.\* The ether, on the other hand, retains all the foreign organic matter which it has dissolved out from the alkaline solution. The ether solution leaves, therefore, upon spontaneous evaporation, a trifling faint yellow residue, of a nauseous odor, and containing a small quantity of conine sulphate, if that base were present.

1110. *Mix the acid solution* (which will contain one or all of the following bases if they are present, as their sulphates are entirely insoluble in ether—sulphates of ammo-

\* Sulphate of conine is not quite insoluble in ether, a little of this alkaloid will therefore remain in the ether solution; the greater part, however, will remain in the aqueous acid solution.

nia, nicotine, aniline, picoline, and petinine; and the solution will also contain the greater part of the conine, if that base is present) with a concentrated solution of  $\text{NaHO}$  or  $\text{KHO}$  in excess, then agitate and exhaust the mixture with pure ether, which will dissolve the liberated bases, including ammonia; the ether solution is drawn off, and then allowed to evaporate at as low a temperature as possible;\* almost all the ammonia volatilizes with the ether, whilst the alkaloid remains as residue. To eliminate the last traces of ammonia, the vessel containing the alkaloid is placed for a few minutes in a vacuum over  $\text{H}_2\text{SO}_4$ ; the alkaloid then remains in a state of purity, and the analyst must determine by appropriate tests what alkaloid it is.

1111. *A non-volatile alkaloid has been indicated in the trial sample.* Let the ethereal solution from which the trial sample was taken evaporate spontaneously, dissolve the residuary impure alkaloid in a little water containing some  $\text{H}_2\text{SO}_4$ , and then shake the solution repeatedly with ether, which will dissolve the foreign matters present, and will not dissolve the sulphates of the alkaloids. Remove the ether solution, and then add to the *aqueous acid solution*  $\text{Na}_2\text{CO}_3$  in excess, and then add some ether immediately and shake repeatedly (the ether dissolves the liberated alkaloid); draw off the ether solution and let it evaporate, when the alkaloids which were held in solution by the ether will be left in a very pure state, and, to a great extent, in the crystalline form; the analyst must now determine by appropriate tests what alkaloid is present.

1112. Uslar and Erdmann employ, instead of absolute alcohol, an oxalic or tartaric acid,  $\text{HCl}$  and amyl-alcohol in the manner described at par. 1104.

1113. *Dialytic method.*—The dialytic method devised by Graham, and noticed at par. 269, may also be advantageously employed to effect the separation of alkaloids from the contents of the stomach, intestines, etc. Acidify with  $\text{HCl}$ , and place the matter in the dialyzer. The alkaloids, being crystalline bodies, dialyze into the outer fluid for the greater part in about twenty-four hours; from this solution they may then, according to circumstances, either be thrown down at once, after concentration by evaporation, or they may be purified according to the general method just given.

1114. Answers to the following exercises must be written out.

\* If conine be present, some of it will evaporate with the ether.

## EXERCISES.

199. Specify the color-tests for morphia, strychnia, and quinine.

200. Name the alkaloids in *nux vomica*, and describe their characteristic reactions.

201. How is iodic acid employed as a test for morphia?

202. How would you examine the contents of a stomach for strychnine? What sort of evidence would you consider necessary to place the presence of the alkaloid beyond doubt?

203. How is morphia detected in organic mixtures?

204. Describe the processes required for the identification of nicotine.

205. Give the tests by which quinine, cinchonine, and quinidine, are distinguished from each other, particularizing the simplest and most certain.

206. Give an account of the preparation and leading properties of meconic acid.

207. What are the distinguishing properties of meconic acid and morphia?

## PART III.

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### OPERATIONS.

#### SOLUTION.

1115. MANY solid bodies, when placed in contact with a liquid, possess the property of becoming thoroughly incorporated with it, by passing into the fluid state. This change is expressed by the term *solution*, and the liquid in which the solid dissolves is called the *solvent*.

1116. Solutions are of two kinds, *simple* and *chemical*. A *simple* or *mechanical solution* is the mere dissolving of a solid in a liquid, no chemical change occurring in either; on the removal, therefore, of the liquid by evaporation, the solid is obtained in its original condition. Common salt dissolved in water affords an illustration of a simple solution.

1117. In a *chemical* solution the solid and fluid combine together, forming an entirely new substance, from which the original solid and fluid can no longer be extracted by mere mechanical operations. Chalk dissolved in  $\text{HCl}$  affords an example of a chemical solution.

1118. The solvent in a simple solution cannot dissolve unlimited quantities of the substance to be dissolved; it can only dissolve certain fixed quantities of the solid, the amount varying with the kind of solid, and the amount of any particular solid varying with the solvent. When the solution contains as great a quantity of the solid matter as it is capable of dissolving, it is said to be *saturated*. A solution is known to be saturated when fresh solid matter of the same sort, on being put into it, remains undissolved. But as fluids dissolve generally larger quantities of a substance the higher their temperature, the term *saturated*, as applied to simple solutions, is only relative, and refers invariably to a certain temperature. From the tendency of heat to diminish the force of cohesion, it naturally results that the solubility of most bodies is increased by heat; this,

however, is not always the case; some bodies, as common salt, are equally soluble in water at all temperatures, whilst, in other cases, the solubility is greater at particular temperatures than either above or below them. The liquids employed as solvents in simple solutions are water, alcohol, ether, oils, etc. The most important solvent is water; the others are only resorted to when the substance to be dissolved is insoluble in that liquid.

1119. "A chemical solution may be *accelerated* by elevation of temperature; and this is, indeed, usually the case, since heat generally promotes the action of bodies upon each other. But the *quantity* of the dissolved body remains always the same in proportion to a given quantity of the solvent, whatever may be the difference in temperature—the combining proportions of substances being invariable, and altogether independent of the gradations of temperature." The liquids which produce chemical solutions are, in most cases, either acids or alkalies.

1120. The process of solution is conducted either in evaporating dishes or test-tubes. The latter are generally employed when the quantity of the solid operated upon is small. The more minutely any substance is powdered, the more its solution is facilitated. Solid substances are generally reduced to powder in mortars.

#### PRECIPITATION.

1121. It is frequently necessary to remove a constituent—it may be either the metal or metalloid of some binary compound, or the acid or base of some ternary one—from the liquid in which the compound is dissolved. This is effected by making it a constituent of some new compound, which is insoluble in the liquid in which the original compound was dissolved. This operation, which is called precipitation, is owing, therefore, to the formation of a new solid substance, which is insoluble in the liquid in which its constituents were dissolved, and which falls, or is precipitated to the bottom, owing to the solid being specifically heavier than the liquid. Occasionally, however, it is lighter, and floats upon the surface. In both cases, the insoluble substance is called the *precipitate*, and the substance producing the precipitation is termed the *precipitant*.

1122. Precipitation is an operation which is constantly practised in the preparation of substances in the manufac-

tory as well as in the laboratory. We also resort to it in the laboratory for the purposes of detecting and separating substances one from another. Thus, if we had a solution which might contain some compound of Ba and Ca: to ascertain whether Ba was present, and, if it was, to separate it from the solution, before ascertaining whether Ca was likewise present, we might add a soluble chromate; if Ba was present,  $\text{BaCrO}_4$  would precipitate, being insoluble in water, whilst  $\text{CaCrO}_4$ , being soluble, would remain in solution. If we were now to add to the clear, filtered solution, some soluble oxalate,  $\text{CaC}_2\text{O}_4$ , being insoluble in water, would precipitate. If the chromate produced no precipitate, there could be no Ba; if the oxalate produced no precipitate, after having separated the Ba (if present), Ca must be absent.

1123. Precipitates are classified, according to their appearances, into *crystalline*, *pulverulent*, *flocculent*, *curdy*, and *gelatinous*. The terms *turbid* and *turbidity* are applied when the precipitate is so small that it cannot be distinguished, except by impairing the transparency of the fluid.

1124. The separation of precipitates from liquids is, with some few exceptional cases, much assisted by the application of heat and agitation. The operation, when performed as an analytical operation, is conducted in test-tubes, which from their transparency admit of an inspection of the process.

#### FILTRATION AND DECANTATION.

1125. These terms are applied to a modification of the same operation, viz., the mechanical separation of fluid from solid matter mixed with them.

#### FILTRATION.

1126. In filtration, the separation of the fluid from the solid matter is accomplished by passing it through filtering paper of a proper size and shape, supported in a funnel. The pores of the paper permit the fluid to pass through; whilst the solid matter, being prevented, remains behind.

1127. To prepare a filter, take a small piece of filtering paper (the best white blotting paper), and fold it twice, from side to side; then round off with scissors the projecting corners, so that the paper may fall wholly within the funnel; moisten the paper when placed within the funnel.



and then carefully pour the liquid to be filtered upon it. The funnel, when large quantities have to be filtered, is supported in one of the rings of the retort stand; but in the ordinary filtrations required in qualitative analysis, it may rest on the mouth of a test-tube. The filter should not project over the edge of the funnel, especially if the substance in the filter requires to be washed. Should the first portions of the liquid which pass through the filter not be perfectly bright, which is frequently the case, they must be returned to the filter, and this must be repeated until it is perfectly bright. The liquid which passes through the filter is called the *filtrate*.

#### DECANTATION.

1128. When the solid particles are very heavy, the supernatant liquid can be perfectly separated, without passing it through a filter, by simply inclining the vessel, so as to allow the fluid to pass away unattended by the precipitate, or by removing the fluid by a syphon.

1129. The separation in this way of a solid from a fluid is called *decantation*.

1130. Too great attention cannot be paid to the washing of precipitates when they are required for further examination. After the precipitate has been thrown upon the filter, a stream of water must be projected from the wash-bottle upon it from time to time, until it is perfectly freed from *soluble matter*; this is soon accomplished if hot water be employed. Hot water may therefore be used in all cases unless the contrary be expressly stated.

#### EVAPORATION.

1131. This process is used for the purpose of obtaining matter in a solid state from solutions. By the aid of heat, the volatile fluid passes off in the gaseous form, whilst the non-volatile matter remains behind.

1132. If the evaporation be conducted slowly, the solid matter will frequently, on being deposited, assume a crystalline form. The operation is then termed *crystallization*.

1133. This operation is frequently conducted for the purpose of obtaining a liquid in a more concentrated form, by volatilizing a portion only of the fluid. Vessels are constructed expressly for the purpose called evaporating dishes.

## DISTILLATION.

1134. This operation, like the former one, consists in the separation of a *volatile* from a *less volatile* fluid, or in the separation of a *liquid* from a *solid*. But in evaporation no attention is paid to the volatilized fluid, whilst in distillation it is frequently the only substance required. A distilling apparatus is therefore so constructed as to allow the evaporated fluid to be collected, which is called the *distillate*. It consists of three parts: 1. A vessel in which the liquid to be distilled is heated. 2. An apparatus in which the vapor is cooled and condensed. 3. A vessel for receiving the distillate.

1135. On a small scale, glass retorts are employed; but in the distillation of large quantities, the stills are usually made of metal.

## IGNITION.

1136. By this operation volatile is separated from non-volatile solid matter; it requires the application of a high temperature, and must be conducted in crucibles. This process is therefore an *evaporation of solid bodies*.

## SUBLIMATION.

1137. By sublimation we effect not only the separation of volatile from less volatile solid matter, but by cooling we bring the volatile matter back to the solid state, and in this state it is called the *sublimate*.

1138. This process is therefore a *distillation of solid bodies*.

## FUSION.

1139. This term is applied to the liquefaction of a solid, by the mere application of heat. It is also used for the decomposition of solids in the "dry way."

1140. By this operation we are able to resolve insoluble substances into forms which admit of solution. This is accomplished by causing their proximate elements to unite with bodies the compounds of which will be capable of solution. Thus  $\text{BaSO}_4$ , which, from its insolubility both in water and acids, resists the action of reagents in the fluid state, is decomposed in this way. It is mixed with

three or four times its own weight of dry  $\text{Na}_2\text{CO}_3$ , and the mixed mass exposed in a crucible for some time to a high temperature. The two salts mutually suffer decomposition when placed in these conditions,  $\text{BaCO}_3$  and  $\text{Na}_2\text{SO}_4$  being formed. If the fused mass be treated with water, the  $\text{Na}_2\text{SO}_4$  dissolves in that liquid, whilst the  $\text{Ba}_2\text{CO}_3$ , being insoluble, remains undissolved, and, after being well washed, may be dissolved in  $\text{HCl}$  or  $\text{HNO}_3$ . The fusion takes place at a lower temperature if a mixture of equal parts of  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  is employed, than if either of the carbonates were used separately.

#### DEFLAGRATION.

1141. This term is applied to all decompositions attended with noise. It also includes the oxidation of a substance by a reagent, in the dry way, on account of the slight explosions which frequently attend this kind of oxidation.

#### THE BLOWPIPE.

1142. The mouth blowpipe is a small instrument which is employed for directing a fine and continuous stream of air into the flame of a candle or lamp. By the flame thus produced two reverse chemical operations may be performed, viz., *oxidation* and *reduction*. The flame is therefore distinguished by these properties into the outer or *oxidizing* flame and the inner or *reducing* flame.

1143. In the *oxidizing* flame, the inflammable vapor is in a state of complete combustion, being supplied and mixed with an excess of atmospheric air. From the high temperature resulting from the perfect combustion of the inflammable vapor, and likewise from the excess of oxygen, all the requisite conditions are present for causing substances with an affinity for that element to enter into union with it.

1144. In the *reducing* or *deoxidizing* flame the inflammable vapor is in an incomplete state of combustion, due to a deficiency of atmospheric air; hence any metallic oxide placed in this portion of the flame is robbed of its oxygen by the inflammable vapor, which requires that element for its combustion.

1145. A *reducing flame* is obtained by keeping the nozzle of the blowpipe in an inclined direction, parallel to the surface of the wick, and just touching the exterior surface of the flame. An *oxidizing flame* is obtained by keeping

the nozzle of the blowpipe at the same inclination as in the former case, and introducing it into the flame to about one-third the breadth of the wick, at such a distance only from the surface of the latter as to obtain a clear, unbroken flame. A weak blast of air is only required for the reducing flame, but a strong blast is required for the oxidizing flame.

1146. The *color* of the reducing flame is *bright yellow* if an oil lamp or candle is used; but if gas is used, it should be of the same blue color as the centre of the oxidizing flame. The color of the oxidizing flame in all cases is a pale-blue, almost invisible by daylight.

1147. "When any substance is submitted to the action of the *reducing flame*, it should be so held as to be entirely surrounded by the reducing flame, and protected from the oxidizing action of the surrounding atmosphere; but this condition being fulfilled, it should be held as near as possible to the point of the flame, in order to gain the greatest amount of heat and prevent any deposition of soot, which would shield the substance from the action of the flame, and would be occasionally attended with other disadvantages."

1148. When a substance is submitted to the action of the *oxidizing flame*, it should be held just beyond the point of this flame if a candle or oil lamp is used; but if gas is used, it should be held at a considerable distance (*viz.*, one-half to three-quarters of an inch) beyond the point of the visible flame.

1149. "As the current of air which is supplied ought to be continuous, its production requires some attention and address. The air is not blown directly from the lungs, but is forced from the mouth by means of the cheeks. The difficulty consists in inspiring and expiring through the nose, while a continued stream escapes from the mouth. This may be attained by attention to the following directions: Inflate the mouth fully, and then, with the lips firmly closed, and the back of the mouth closed by the tongue, breathe freely through the nostrils. While the respiration proceeds, and the mouth is inflated, allow a little air to escape through a very minute opening between the lips, renewing the supply in the mouth by occasionally admitting air from the lungs without interfering with the process of respiration through the nose."—*Parnell*. In attempting this, the student will not, probably, be immediately successful, but a few days' persevering practice will enable him entirely to master this primary difficulty.

1150. *The flame of the blowpipe*.—When coal-gas is

available, it is to be preferred, since it is perfectly free from dirt and grease, and admits of being regulated with the greatest nicety. The gasburner ought to be of an oblong shape instead of round, the current of air being blown lengthways. When gas cannot be procured, an oil lamp or wax candle may be used. An oil lamp proper for blowpipe operations can be obtained at any of the shops where they sell chemical apparatus—it need not, therefore, be described; it will be sufficient to say that it must have a broad and moderately thick wick, and that on each occasion the wick must be trimmed\* before employing the flame for the blowpipe experiments. The best kind of oil for the lamp is pure rape or olive oil. The flame of a wax candle is far inferior in size and intensity to that of a lamp. Bunsen's lamp is described at par. 1167.

1151. SUPPORTS.—Various materials are used as supports for substances during the time they are exposed to the blowpipe flame; the principal are charcoal, platinum wire and foil, and glass tubes. The kind of support is regulated by the change we wish to effect upon the substance under examination.

1152. Charcoal.—The properties which make charcoal so valuable as a material for supports in blowpipe experiments are—1st, its infusibility; 2d, its low conducting power for heat, which permits substances being heated more strongly upon a charcoal than upon any other kind of support; 3d, its porosity, which makes it imbibe readily fusible substances, such as borax, carbonate of soda, etc., whilst infusible bodies remain on the surface; 4th, its power of reducing oxides, which greatly contributes to effecting the reduction of oxides in the inner blowpipe flame.

1153. Charcoal supports are used principally in the reduction of metallic oxides, etc., or in trying the fusibility of bodies. The substance to be subjected to the blowpipe flame—which, if in powder, should be previously moistened with a little water to make it cohere—is placed in a shallow hole made in the charcoal either with a knife or with a proper charcoal borer, and the charcoal is so held that the flame may impinge upon it at an angle of about 20 degrees. Metals that are volatile at the heat of the reducing flame evaporate wholly or in part upon the reduction of their oxides; in passing through the outer flame the metallic

\* The wick must be evenly cut and perfectly free from all extraneous fibres.

fumes are reoxidized, and the oxide formed is deposited around the portion of the matter upon the support. Such deposits are called incrustations. Many of these exhibit characteristic colors leading to the detection of the metals.

1154. Charcoal made from light woods—as the alder and pine—is the best for blowpipe experiments. It must be well-burned; it must be compact and free from crevices; it must not scintillate, smoke, or burn with flame; and it must, of course, be perfectly dry. It should be cut by a small-toothed saw into pieces about six inches in length and from one to two inches in breadth, having a flat smooth surface at right angles to the rings of growth. It is this surface which is always to be used; and a good piece of charcoal may be made to serve for repeated experiments by simply filing off the used surface, and exposing a new one after each operation. As it is very difficult to get charcoal sufficiently good for blowpipe experiments, Mr. John J. Griffin has provided an excellent substitute, an account of which is given in pars. 1160 to 1167.

1155. *Platinum*.—Platinum wire, and occasionally platinum foil, is used in all oxidizing processes before the blowpipe, and also when fusing substances with fluxes, with a view to try their solubility in them and to watch the phenomena attending the solution and mark the color of the bead; lastly, also to introduce substances into the flame, to see whether they will color it.

1156. The ends of the wire are twisted into a small loop (fig. 5), and when required for use, the loop is moistened with a drop of water, then dipped into the powdered flux (when a flux is used), the portion adhering to the wire is then

Fig. 5.



exposed to the flame of a gas or spirit-lamp, when fused, and whilst still hot, it is dipped again into the powdered flux, and this is continued until the loop is completely filled with the flux after it has been fused. The bead when cold is moistened again, and a small portion of the substance to be examined put on and made to adhere to it by the action of a gentle heat. The loop is then finally exposed, according to circumstances, to the inner or to the outer blowpipe flame.

1157. A great many metallic oxides dissolve in borax,

forming colored glasses. If any metallic arsenides or sulphides are present in the substance which has to be examined with borax, the substance must be roasted by the method described in the next par. before making the examination with borax; and it is frequently advantageous, before roasting the powdered substance, to mix it with a little powdered charcoal, so as to prevent the formation of sulphates and arseniates.

1158. *Glass tubes*.—Tubes of hard German glass of about a quarter of an inch internal diameter, five or six inches long, and open at both ends, are used in blowpipe experiments principally for roasting substances containing sulphur, arsenic, selenium, antimony, tellurium, etc., which, when heated with access of air, evolve fumes which may be recognized by color, odor, and chemical reaction.

1159. *Small Glass Bulbs*, or, what answer equally well, glass tubes closed at one end, of about two and a half to three inches long, and from one-eighth to one-fourth of an inch internal diameter, are employed to test substances for water, mercury, sulphur, or other bodies which are volatilized by the application of heat without the access of air. The volatile products collect in the neck of the bulb or tube, and may be judged of by their color, odor, etc.

1160. *Griffin's substitute for charcoal*.—"The blowpipe experiments that require the assistance of charcoal may be divided into two classes. In the first class may be named the formation of beads with microcosmic salt, the trial of fusibility *per se*, and the roasting of the metallic compounds that contain such volatile elements as sulphur and arsenic. The second class of experiments is restricted to the fusion of minerals or metallic compounds with carbonate of soda, or with soda and borax, for the purpose of effecting particular combinations, or of procuring their metals in a state of regulus. For these two classes of experiments I make use of two different composition supports, the first of which I call *Supports for Fusions*, and the second, *Supports for Reductions*. They are alike in appearance. Each consists of two parts—an upper or combustible portion, and a base or incombustible portion. The former is the proper substitute for the ordinary charcoal, the under portion acting only as a crucible, in which the combustible portion is contained. I shall first describe the composition and formation of the supports, and afterwards show the way to use them.

1161. "The incombustible portion of both supports is

made of fine pipeclay and charcoal powder, mixed in equal parts by weight with as much water, slightly thickened with rice paste, as is sufficient to form a stiff plastic mass.

1162. "The combustible portion of the *Support for Fusions* consists of—

"Charcoal, in fine powder,	-	12	parts.
Rice flour,	- - - -	$\frac{1}{2}$	"
Water, about	- - -	8	"

The rice is boiled in the water to form a paste, with which the charcoal is afterwards mixed into a mass of the consistence of dough.

1163. "The upper part of the *Support for Reductions* consists of the following mixture:—

"Charcoal, in fine powder,	-	9	parts.
Carbonate of soda, crystallized		2	"
Borax, crystallized,	- -	1	"
Rice flour,	- - - -	$\frac{1}{2}$	"
Water, about	- -	8	"

The water is boiled, the soda and borax are dissolved in it, and the rice is then added to form a paste, with which the charcoal is finally incorporated, and the whole well kneaded into a stiff mass. The mould in which these compositions are pressed to form the supports is made of boxwood.\*

1164. "The principal points which require attention to insure success in this process are to have the materials in the state of a very fine powder, and the moist compositions of a proper degree of consistency. If they are too soft, the support will not quit the mould without losing its form; if too dry, the particles of the support will not cohere. The proper state is found after a few trials. It is most convenient to begin by making the mixture too soft, and then drying it slowly till it is found to be hard enough to work easily. The composition is rolled into balls with the fingers. The moulds should be kept clean, and the forming parts of the pestle for the charcoal composition, and the ring, should be oiled. The point of the pestle for the clay composition must not be oiled, because grease prevents the adhesion of the combustible portion of the clay base. A pestle made on purpose for the operation, is used to remove

\* These moulds, and every other part of the apparatus, are sold by Mr. Griffin, and, I have no doubt, can be procured through any of the other dealers in chemical apparatus.



the finished support from the mould, by pressure on the clay foundation.

1165. "When the support is taken from the mould, it is placed on a hot plate or sand-bath to dry, after which the rough edges are taken off by a rasp. It is then ready for use. The bottoms of *supports for reductions* are painted with red ochre mixed with rice paste, to distinguish these from the other kind. The size I have fixed upon is as follows: height, half an inch; diameter at top, half an inch; at bottom, two-fifths of an inch. The weight is about 16 grains, consisting of 10 grains of clay crucible, and 6 grains of combustible matter. I have tried several other sizes, but this I find to be the most generally convenient. Nevertheless, a higher temperature can be produced upon a smaller support; and I find that large masses of charcoal are not essential, since many blowpipe experiments can be finished during the combustion of only two grains of charcoal. When in use, they are supported by a handle made of wire, turned into the form of a ring; a piece of tobacco pipe can be used for the handle of the wire support.

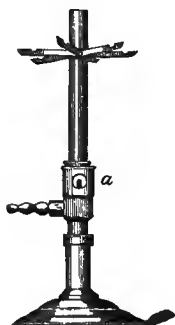
1166. "The following is the method of using these supports.

"Firstly, the surface of one of the supports for fusion is heated before the blowpipe flame. The support continues to burn like an ordinary pastile, till it is consumed down to the clay; in this respect the support has a superiority over common charcoal, which soon ceases to burn when removed from the fire. The ignited support is then to be rested upon a porcelain capsule, and a quantity of microcosmic salt, sufficient to form a bead, is placed on its red-hot surface. The salt instantly melts, and sinks into the central cavity, so as to form a bead; the heat, the form, and the smoothness of the surface of the support, facilitating this part of the process. The salt is then heated before the blowpipe, till it is converted into a transparent, colorless bead. The support is again placed on the porcelain capsule, and the metallic substance intended to be incorporated with the bead is added to it. The support continuing to be red-hot, and the bead consequently continuing soft, the substance so added is immediately absorbed, and its loss by dispersion prevented; whereas, upon common charcoal the fused salt solidifies soon after it is removed from the flame, and the substance added for examination, not adhering to it, is often blown away by the first blast from the blowpipe jet. The bead is now again fused, till the sub-

stance added to it is decomposed, and the resulting glass is observed to fuse quietly. It is then ready for examination; but it is sunk in the bottom of the hollow of the support, and cannot be seen by transmitted light, unless the projecting sides of the support be removed. This is effected as follows: the support is placed, as before, on the porcelain capsule, and the operator blows with his mouth, without the blowpipe, strongly down upon its surface. The pastile then burns away rapidly, and the force of the blast disperses the ashes, until the whole rim of the support is consumed. The bead then appears situated on the summit of a cone, and can be examined either by reflected or transmitted light. It is also in a position adapted for exposure to the different action of the oxidating and reducing flames, so as to have the character of the included metal fully developed. If, finally, the charcoal is allowed to burn wholly away, the colored bead can be lifted from the ashes and preserved in a glass tube for subsequent examination and comparison.

"Secondly, if the surface of one of the *supports for reductions* be heated before the blowpipe, it becomes at first like the simple charcoal support; but in proportion as the charcoal is consumed, the fluxes which were mixed with it, and which are not volatile, concentrate and fuse upon the surface of the residue. If, therefore, a reducible metallic compound is heated upon such a support, it becomes at once exposed to the reducing action of the high temperature, of the nascent oxide of carbon, and of the carbonate of soda, whilst any earthy matter that it may contain is vitrified by the attendant borax."—*Griffin*.

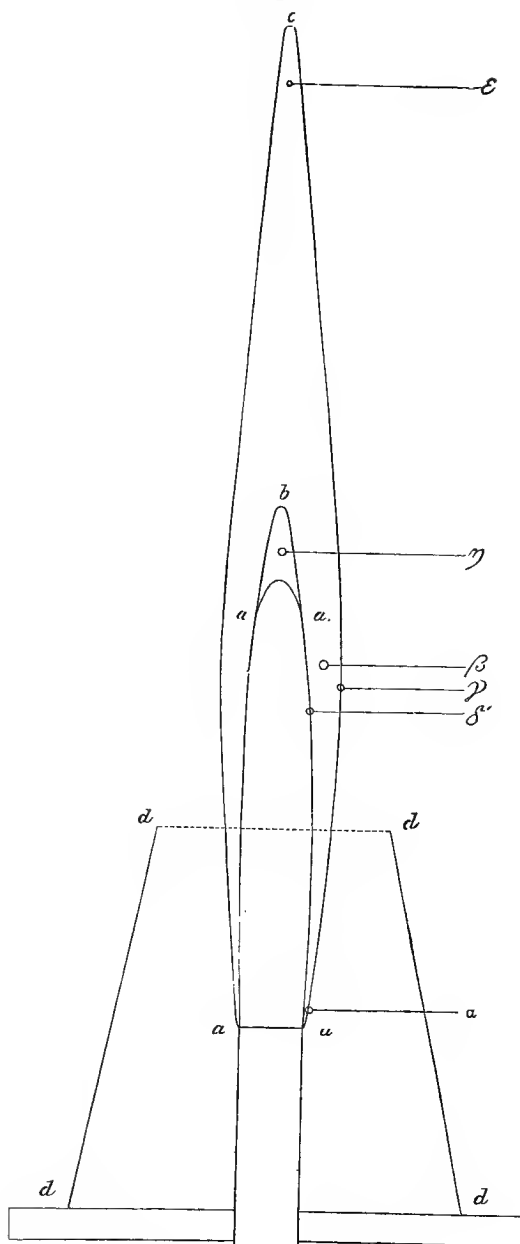
Fig. 6.



1167. *Bunsen's gas-lamp*.—This gas-lamp with non-luminous flame is represented in Fig. 6, and must be made exactly to scale,  $3\frac{1}{2}$  times as large as the drawing. It must be furnished with a cap at *a* for closing and opening the draught-holes, so as to be able to regulate the supply of air for every dimension of the flame. The conical chimney, *ddd d*, Fig. 7, must also be made of such a size that the flame burns perfectly steady. Fig. 7 represents this flame of

its natural size. It is composed of the following three chief divisions:—

Fig. 7.



A. The *dark cone*,  $a a a$ , containing the cold unburnt gas mixed with about 62 per cent.

B. The *flame mantle*,  $a c a b$ , formed of the burning coal-gas mixed with air.

C. The *luminous point*,  $a b a$ , not seen when the lamp is burning with the draught-holes open, but obtained of the size required for the reactions by closing these holes up to a certain point.

The following six points in the flame are used in the reactions:—

1. The *base of the flame* lies at  $\alpha$ ; its temperature is comparatively very low, as here the burning gas is cooled by the upward current of cold air, and much heat is absorbed by the cold end of the metal tube. If mixtures of flame-coloring substances are held in this part of the flame, it is often possible to vaporize the most volatile constituent, and thus in the first few moments to obtain tints which cannot be observed at higher temperatures, because they then become masked by colors produced by the volatilization of the remaining substances.

2. The *zone of fusion* lies at  $\beta$ , somewhat above the first third of the flame in height, and midway between the inner and outer limits of the mantle at the point where the flame is thickest. This is the point in the flame which possesses the highest temperature, and it is therefore used in testing substances as regards their melting-point, their volatility, emissive power, as well as for all processes of fusion at high temperatures.

3. The *lower oxidizing flame* lies at  $\gamma$ , in the outer margin of the zone of fusion, and is especially suitable for the oxidation of substances dissolved in beads of fused salts.

4. The *upper oxidizing flame* at  $\delta$  is formed by the highest point of the non-luminous flame, and acts most powerfully when the draught-holes of the lamp are wide open. This flame is suited for the oxidation of larger portions of substance, for roasting off volatile-oxidation products, and generally for all those cases of oxidation in which an excessively high temperature is not needed.

5. The *lower reducing flame* lies at  $\delta$ , on the interior edge of the mantle next to the dark central zone. As the reducing gases at this point are mixed with unburnt atmospheric oxygen, many substances remain here unaltered which become deoxidized on exposure to the upper reducing flame. This point of the flame gives, therefore, very valuable reactions which cannot be obtained with the

blowpipe. It is especially available for reductions on charcoal, and in beads of fused salts.

6. *The upper reducing flame* is formed by the luminous point  $\eta$ , produced over the dark zone when the admission of air is lessened by the gradual closing of the draught-holes (Fig. 6, *a*). If this luminous point is made too large, it will be found that a test-tube filled with cold water becomes covered with a film of lampblack: this never ought to occur. This flame contains no free oxygen, is rich in finely divided incandescent carbon, and hence it possesses far more powerful reducing powers than the lower reducing flame. It is especially available for reducing metals when it is desired to collect them in the form of films.

#### METHOD OF EXAMINATION IN THE VARIOUS PARTS OF THE FLAME.

##### *A. Behavior of the Elements at High Temperatures.\**

1168. This is one of the most important reactions which can be employed for the detection and separation of substances. The possibility of producing, with the flame of the lamp alone, a temperature as high as or higher than that of the blowpipe depends upon the fact that the radiating surface of the heated body be made as small as possible. The arrangement for bringing the substances into the flame must therefore be on a very small scale. The platinum wire upon which the substance is heated must scarcely exceed the thickness of a horsehair, and one decimetre in length of the wire must not weigh more than 0.034 grm. It is impossible to obtain the results hereafter detailed if a thicker wire than this is employed. Substances which act upon platinum, or which will not adhere to the moistened surface of the metal, are held in the flame upon a thin thread of asbestos, of which a hundred may be obtained from one splinter of the mineral. These threads must not exceed in thickness one-fourth of that of an ordinary lucifer-match. Decrepitating substances are ground to the finest powder on the porcelain lamp-plate with the elastic blade (*a*) of the knife (Fig. 8) and drawn up on to a moistened strip of one square centimetre of filter paper.

\* For further information with regard to the flame reactions the student is referred to the translation of Bunsen's paper by Professor Roscoe in the "Philosophical Magazine," for 1867.

If the paper is then burnt, being held with the platinum forceps, or, better, between two rings of fine platinum wire, the sample remains as a coherent crust, which now may without difficulty be heated in the flame.

Fig. 8.



Fig. 9.

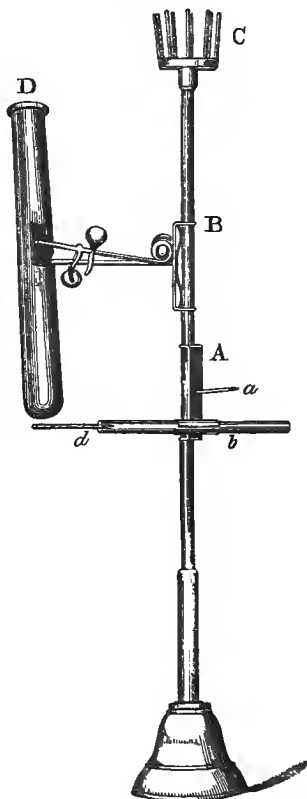


Fig. 10.



1169. If the substance requires to be heated in the flame for a long period, the holder (Fig. 9) is used. The arm (*a*) is fastened to the carrier (*A*), so fixed on the stand by a spring (as seen at *B*) that it can be moved both horizontally and vertically. The glass tube (Fig. 10) is held on this arm (*a*), and the fine platinum wire fused on to the

tube thus held in the flame. The splinters of asbestos are stuck into the glass tube (*b*), which slips into the holder, and may then be moved with the carrier (*A*). The carrier (*B*) carries a spring-clamp for holding test-tubes which have to be heated for a considerable time in a particular part of the flame. The little turn-table (*C*) contains nine upright supports to hold the wire tubes (Fig. 10) employed in the experiments. By means of these arrangements a particle of the substance under examination is brought into the flame, and its behavior in the coldest and hottest parts of the flame is ascertained, the substance being examined with a lens after each change of temperature. The following six different temperatures can be obtained in the flame, and these points may be judged of by observing the tints attained by the thin platinum wire:—

1. Below a red heat. .
2. Commencing red heat.
3. Red heat.
4. Commencing white heat.
5. White heat.
6. Strong white heat.

It is scarcely necessary to remark that these different temperatures must not be ascertained by the glow of the substances themselves, as the luminosity of different bodies depends not only upon the temperature, but also mainly upon their specific power of emission.

1170. The following phenomena are observed when a sample of a substance is heated:—

1. *Emission of Light*.—The emissive power of substances is ascertained by placing them on the platinum wire in the hottest part of the flame. The sample is of weak emissive power when it is less luminous than the platinum wire, of a mean emissive power when both appear about equally luminous, and of strong emissive power when the intensity of the light which it emits is greater than that from the platinum. Most solid bodies emit a white light, others (as, for instance, erbia) colored light.

Some bodies, such as many osmium, carbon, and molybdenum compounds, volatilize and separate out finely divided solid matter, which renders the flame luminous. Gases and vapors always exhibit a smaller power of emission than fused substances, and these generally less than solid bodies. The form of the substance under examination must always

be noted, as the emissive power depends upon the nature of the surface: thus compact alumina, obtained by slowly heating the hydrate, possesses only a moderate emissive power, whereas the porous oxide prepared by quick ignition of the sulphate possesses a high power of emission.

2. *The melting point* is determined by using the six different temperatures already mentioned. At every increase of temperature the bead is examined with the lens to see whether the volume is decreased or increased, whether bubbles are given off on melting, whether on cooling the bead is transparent, and what changes of color it undergoes during the action of the heat or on afterwards cooling.

3. *The volatility* is ascertained by allowing equally heavy beads of the substance, placed on a platinum wire, to evaporate in the zone of fusion, and observing the time, by means of a metronome, which the bead takes to volatilize. The point at which the whole of the substance is converted into

Fig. 11.



vapor can be ascertained with great accuracy, often to a fraction of a second, by the sudden disappearance of the coloration of the flame. The platinum wire upon which the substance is weighed is protected from the moisture of the air by insertion in a tube (Fig. 11). If we know the weight of the tube and wire, the right weight of substance can easily be attached, either by volatilizing a portion or by fusing some more substance on to the bead, and thus making it lighter or heavier. The experiments are best made with one centigramme of substance. The position in the flame where the highest constant temperature exists can be found by moving a fine platinum wire, fixed on a stand and bent at its point at a right angle, slowly about the zone of fusion, and noting the point where it glows most intensely. The beads to be volatilized are then most carefully brought into the flame at the same distance from the point of this wire.

Care must also be taken that the dimensions of the flame do not undergo change from alterations in the pressure of the gas whilst the experiments are going on.

4. *Flame-coloration*.—Many substances which volatilize in the flame may be detected by the peculiar kinds of light which their glowing gases emit. These colorations appear in the upper oxidizing flame when the substance causing



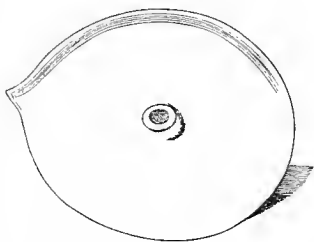
them is placed in the upper reducing flame. Mixtures of various flame-coloring substances are tested in the lowest and coldest part of the flame; and here it is often possible to obtain for a few moments the peculiar luminosity of the most volatile of the substances unaccompanied by that of the less volatile constituents.

### B. Oxidation and Reduction of Substances.

1171. In order to recognize substances by the phenomena exhibited in their oxidation and reduction, and to obtain them in a fit state for further examination, the following methods are employed:—

1. *Reduction in glass tubes* is especially employed for the detection of Hg, or for the separation of S, Se, P, etc., when in combination with Na or Mg. A stock of very thin glass tubes is prepared, each 2 to 4 millims. in width and 3 centims. in length; forty of these are easily made out of one ordinary-sized test-tube, by softening the glass before the blowpipe, and then drawing it out until the requisite size of tube is obtained. This long tube is then cut up with a diamond into pieces 6 to 8 centims. long, and each of these again divided into two over the lamp, and the closed ends neatly rounded. The sample, having been finely powdered with the knife-blade (Fig. 8, *a*) on the porcelain plate (Fig. 12), is treated in a tube either by itself, or with a mixture of carbon and soda, or with Na or Mg. A piece of magnesium wire, a few millims. in length, is for this purpose pushed down into the powdered sample contained in the glass tube; the sodium is carefully freed from rock oil, and rolled out between the fingers to a small cylinder, which is then surrounded by the powdered substance. The best

Fig 12.



form of carbon is the soot from turpentine, which has been deposited upon the outside of a basin filled with cold water. As soon as the small tube containing the perfectly dry sample has been heated to the point of fusion of the glass, when generally an ignition inside the tube is noticed, it is allowed to cool and then placed upon the porcelain plate

covered by a piece of paper and crushed to powder with the knife, for the purpose of further examining the products of reduction.

2. *Reduction on splinters of Charcoal.*—In this way the metal can be obtained in small globules, or as a porous mass, from quantities often less than a milligramme of the sample.

A transparent crystal of sodic carbonate is brought near to the outside of the flame, and a common wooden lucifer-match then rubbed over two-thirds of its length with the drops of fused salt. If the match is then turned upon its axis through the flame, the carbonized wood becomes surrounded with a crust of solid sodic carbonate, which, on heating in the zone of fusion, melts, and is absorbed by the carbon. A splinter of charcoal is thus obtained, which is prevented from burning by its glaze of soda. A mixture of the substance is then made with the knife upon the hand with one drop of the melted soda-crystal, and a portion of this, of the size of a mustard seed, placed upon the point of the splinter. As soon as this has been melted in the lower oxidizing flame, it is passed through a part of the dark interior zone to the hotter portion of the lower reducing flame. The point at which the reduction occurs is easily seen by the violent effervescence of the soda; and this is after a time stopped by bringing the splinter into the dark zone. In order to isolate the reduced metal, the end of the splinter is broken off and rubbed up with a few drops of water in a small agate mortar, when the metallic particles are generally visible without removal of the carbon. For further examination, the carbon and soda can be easily removed by several careful washings, and the particles transferred to a small piece of curved glass cut out from an old flask,\* in which they are again washed by decantation, the last drops of water removed by suction with a piece of filter-paper, and the metallic particles dried at a moderate heat. A few tenths of a milligramme of the metal is generally sufficient to yield a solution with which all the characteristic precipitations can be accomplished, the reagents being contained in capillary glass threads, dropped into the solution by the milligramme, and the effect thus produced ascertained by examination with a lens. Iron, cobalt, and nickel, which do not fuse to globules on the

\* Watch-glasses crack much too readily to be used for such experiments.

splinter, are withdrawn from the agate mortar by means of the point of the magnetized blade (Fig. 8, *b*), washed with water, and dried high above the flame on the point of the knife. If the blade be then tightly drawn between the upper part of the thumb and the lower part of the first finger, and if the point of the blade be then approached to the metallic particles on the finger, they jump from the hand to the blade, forming a brush-like bundle, which can be conveniently examined by the lens, and by touching with a melted borax bead can be transferred in suitable quantities. The portion of metal remaining on the knife is rubbed on to a small piece of filter-paper, a drop of acid added, and the paper warmed over the flame so as to allow the metal to dissolve; this solution can then be further examined with various reagents.

3. *Films upon Porcelain.*—Those volatile elements which are reduced by carbon and hydrogen can be deposited from their compounds as films on porcelain either in the elementary state or as oxides. Such films can be extremely easily converted into iodides, sulphides, and other compounds, and thus may be made to serve as most valuable and characteristic tests. The films are composed in the centre of a thick layer, which on all sides gradually becomes thinner until the merest tinge is reached; it is therefore necessary to distinguish between “thick” and “thin” parts of the films. Both exhibit in their variation of thickness all the tints of color characteristic of the substance under different circumstances of division. One-tenth up to one milligramme is in many cases sufficient for these reactions. Many surpass Marsh’s arsenic test in delicacy and certainty, and approach in this respect the spectrum-analytical methods.

The following films can be obtained:—

(*a*) *Metallic films* are prepared by holding in one hand a particle of the substance on an asbestos-thread in the upper reducing flame, which must not be too large, whilst with the other hand a glazed porcelain basin, 1 to 2 decimetres in diameter, filled with cold water, is held close above the asbestos-thread in the upper reducing flame. The metals separate out as dead-black or brilliantly-black films of varying thickness. Even Pb, Sn, Cd, and Zn yield in this way films of reduced metal, which by mere inspection cannot be distinguished from the soot separated out on the porcelain by a smoky flame. By means of a glass rod, these films can be touched with a drop of dilute  $\text{HNO}_3$ , contain-

ing about 20 per cent. of real acid; and the various degrees of solubility of the films serves as a distinguishing characteristic.

(b) *Oxide-films* are obtained by holding the porcelain basin filled with water in the *upper oxidizing flame*, the rest of the operation being the same as in the production of the metallic films. If only a very small quantity of the sample can be employed, care must be taken to lessen the size of the flame, in order that the volatile products may not be spread over too large a surface of porcelain.

The film of oxide is examined as follows:—

(α) The color of the thick and thin film is carefully observed.

(β) The reducing action or otherwise of a drop of stannous chloride is noted.

(γ) If no reduction occurs, NaHO is added to the stannous chloride until the precipitated hydrate redissolves, and then it is to be observed whether a reduction occurs.

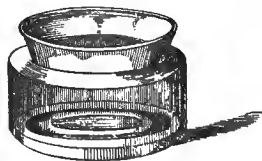
(δ) A drop of perfectly neutral silver-nitrate is rubbed over the film with a glass rod, and a current of ammoniacal air is blown over the surface from a small wash-bottle containing ammonia solution, and having the mouth tube dipping under the liquid and the exit-tube cut off close below the cork. If a precipitate is formed, the color is observed, and the solubility or alteration, if any, noticed which occurs when the current of alkaline air is continued, or when a drop of ammonia-liquor is added.

(b) *Iodide-films* are simply obtained from the oxide-films by breathing on the latter upon the cold basin, which is then

placed upon the wide-mouthed well-stoppered glass (Fig. 13) containing fuming hydriodic acid and phosphorous acid derived from the gradual deliquescence of phosphoric triiodide. When the mixture no longer fumes, owing to absorption of moisture, it is easy to render it again fuming by adding a little phos-

phoric anhydride. Other films, often containing both iodides of a metal, and therefore frequently less regular in color and appearance, may be easily obtained by smoking the oxide-film with a flame of alcohol containing iodine in solution placed upon a bundle of asbestos-threads and held under the basin. If any iodine be condensed on the basin

Fig. 13.



with the HI, it can easily be removed by gentle warming and blowing.

The examination of the film is conducted as follows:—

(a) The solubility of the film is examined simply by breathing upon it when the basin is cooled; the color then either changes or entirely disappears, the film being dissolved in the moisture of the breath. If the basin be gently warmed, or if it be blown upon for some distance, the film again becomes visible by the evaporation of the moisture in the current of air.

(β) The ammonia compound of the iodide is formed by blowing ammoniacal air upon it, and noticing whether the color of the thick and thin films alters quickly, slowly, or not at all. The different colors reappear at once if the basin be held for a few moments over an open bottle containing fuming HCl.

(γ) The iodide-films generally give the same reactions as the oxide-films with silver-nitrate and ammonia, with stannous chloride, and with caustic soda.

(b) The *sulphide film* is most easily obtained from the iodide-film by blowing upon it a current of air saturated with ammoniac sulphide, and removing the excess of sulphide by gently warming the porcelain. It is advisable to breathe on the film from time to time whilst the current of sulphuretted air is being blown on the basin. The experiments to be made with this film are:—

(a) The solubility or otherwise in water is ascertained by breathing on to it, or by addition of a drop of water. The sulphides often possess the same color as the iodide-films; they may, however, generally be distinguished by their insolubility on breathing.

(β) The solubility of the sulphide in ammoniac sulphide is ascertained by blowing or dropping.

(b) *Films on Test-tubes*.—Under certain circumstances it is advisable not to collect the film on porcelain, but upon the outside of a large test-tube (Fig. 9, D); this method is especially used when it is needed to collect larger quantities of the reduction film for the purposes of further examination. The fine asbestos-thread with the sample of substance is held on the glass tube (b) before the lamp so that it is placed at the height of the middle of the upper reducing flame, and the test-tube fixed so that the lowest point is just above the end of the asbestos-thread. If the lamp be now pushed under the test-tube, the substance and the asbestos-thread are in the reducing flame. By repeating

this operation the film can be obtained of any wished-for thickness; some pieces of marble are in this case placed in the test-tube, to prevent the water from being thrown out of the tube by percussive boiling.

### III. THE REACTIONS OF THE ELEMENTS.

1172. The elements, which can easily be recognized by their flame reactions, are arranged in the following groups and sub-groups according to their behavior in the reducing and oxidizing flames:—

A. Elements which are reducible to metal and are deposited in films.

1. Films scarcely soluble in cold dilute nitric acid—tellurium, selenium, antimony, arsenic.
2. Films slowly and difficultly soluble in cold dilute nitric acid—bismuth, mercury, thallium.
3. Films instantly soluble in cold dilute nitric acid—cadmium, zinc, indium.

B. Elements reducible to the metallic state, giving no film.

1. Not fusible to a metallic bead.
  - a. Magnetic—iron, nickel, cobalt.
  - b. Non-magnetic—palladium, platinum, rhodium, iridium.
2. Fusible to metallic beads—copper, tin, silver, gold.

C. Elements most easily separated and recognized as compounds—tungsten, titanium, tantalum and niobium, silicon, chromium, vanadium, manganese, uranium, sulphur, phosphorus.

### APPARATUS REQUIRED IN PHOTO-CHEMICAL EXPERIMENTS.

1173. A large number of substances are volatilized when a small particle of the substance in the solid state is introduced into the inner flame of a gas or spirit-lamp. Many of these substances in volatilizing color the outer flame, and as the color imparted to the flame is in most cases different and distinct for each substance, the coloration of the flame has long been employed in chemical analysis as a test for many substances. Thus—Soda and its salts impart to the flame a yellow, potash and its salts a violet, strontia and its salts a crimson color. The intensity of the color of the salts of the same base, varies with their volatility,

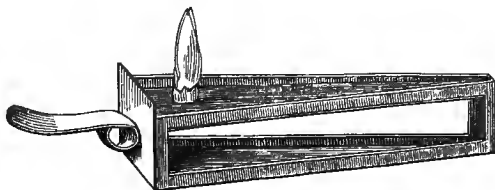
the most volatile of the salts producing the most intense coloration. Difficultly volatile salts produce only a slight, and non-volatile salts no coloration; thus, with silicates and other non-volatile compounds, such as are met with in nature, it is often difficult to detect 3 or 4 per cent. of the alkalies. In such cases the coloration may frequently be produced by adding some other substance which has the power of decomposing the compound under examination, and forming, with the substance we wish to detect, a compound which will volatilize at the temperature of the flame. If we add, for instance, to silicates containing only 3 or 4 per cent. of the alkalies, a little *pure* gypsum, this will decompose the silicate, a volatile alkaline sulphate, which will impart a color to the flame, being formed.

1174. As the color produced by one substance interferes or entirely obscures that produced by another, we were formerly unable to detect more than one body in a mixture of substances by means of the color imparted to the flame. This defect has lately been overcome by looking at the colored flame through colored media, as colored glasses and colored liquids, which intercept the color produced by one substance, whilst they allow the color produced by another substance to pass. Thus, the yellow color produced by sodium compounds obscures the violet produced by potassium ones; Cartmell, who was the first to employ colored media, proposed, in order to detect potash in the presence of soda by means of the colored flame, to view the flame through a blue glass stained with cobalt: through this colored glass no colored rays from soda (or lithia) can pass, but it admits those peculiar to potash.

1175. A solution of indigo can also be employed for the same purpose, Cartmell, for instance, detected lithia in the presence of soda and potash, by comparing the mixed color of the flames of those bases with that of the flame of pure potash, when both are viewed through an indigo solution. Bunsen has found that the discrimination of these bases in presence of each other is more easily effected by observing the *succession of changes of color*, which the mixed flame produced by these substances experiences when the rays reach the eye after passing through gradually thicker layers of an indigo solution. For this purpose a hollow plate glass prism (Fig. 14) is used, filled with indigo solution; it is 40 millimetres high, and its principal section is a triangle, with two sides of 150 millimetres, and the other of 35 millimetres. The indigo solution is made by dissolv-

ing 1 part of indigo in 8 parts of fuming sulphuric acid, diluting with 1500 to 2000 parts of water, and filtering.

Fig. 14.



1176. In the following experiments the prism was moved horizontally before the eye, so that the rays of the flame always passed through gradually thicker layers of the medium. The alkaline substances, brought singly into the melting-space, exhibited the following changes:—

1. *Chemically pure*  $\text{CaCl}_2$  produces a yellow flame, which, even with very thin layers of the indigo solution, passed through a tinge of violet into the original blue lamp flame.

2. *Chemically pure*  $\text{NaCl}$ , the same.

3. *Chemically pure*  $\text{K}_2\text{CO}_3$  or  $\text{KCl}$  appears of a sky blue, then violet, and at last of an intense crimson red, even when seen through the thickest layers of solution. Admixtures of soda or lime do not hinder the reaction.

4. *Chemically pure*  $\text{Li}_2\text{CO}_3$  or  $\text{LiCl}$  gives a carmine-red flame, which, with increasing thickness of the medium, becomes gradually feebler, and disappears before the thickest layers pass before the eye. Lime and soda are also without influence on this reaction.

1177. Merz has proposed employing, in addition to the cobalt blue glass, a *violet*, a *red*, and a *green*, glass; the violet glass is tinted with manganic oxide; the red glass (partly colored and partly uncolored) with cuprous oxide, and the green glass with ferric and cupric oxides. The common colored window glass will generally be found to answer the purpose of the green glass.



## REAGENTS.

## 1178.—LIST OF THE REAGENTS EMPLOYED IN THE FLUID STATE.

1.  $\text{HCl}$ , *Hydrochloric acid* (muriatic acid), if *pure*, is perfectly colorless, and leaves no residue when evaporated; its sp. gr. should be 1.2. The substances with which it is generally contaminated are Fe, As, and  $\text{H}_2\text{SO}_4$ . It may also contain Cl and  $\text{SO}_2$ .

If it gives, after dilution with distilled water, a precipitate with  $\text{BaCl}_2$ ,  $\text{H}_2\text{SO}_4$  is present. If it turns yellow on evaporation, or if, after adding  $\text{NH}_4\text{HO}$  in excess, then acidifying with acetic acid, it gives a blue color after the addition of a solution of potassic ferrocyanide, it contains  $\text{Fe}'''$ . If it imparts a blue tint to a solution of KI mixed with starch paste, it contains Cl, and if it discolors a fluid made faintly blue with iodide of starch, it contains  $\text{SO}_2$ . Examine it for As by Marsh's test, described in the fifth group of bases.

Dilute one part of the concentrated acid with two parts of water.

2.  $\text{HNO}_3$ , *Nitric acid* (aqua fortis), when free from non-volatile matter, leaves no residue on evaporation; its sp. gr. should be 1.517. The impurities often found in it are  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$ .

If, after dilution with distilled water, it gives a precipitate with  $\text{BaCl}_2$ ,  $\text{H}_2\text{SO}_4$  is present; and if the diluted acid gives a precipitate with  $\text{AgNO}_3$ ,  $\text{HCl}$  is present.

Dilute one part of the concentrated acid with two of water.

3. *Nitro-hydrochloric acid* (aqua regia) is prepared by adding four parts of concentrated hydrochloric acid to one of concentrated nitric acid.

"Nitric acid and hydrochloric acid decompose each other, the decomposition mostly resulting, as *Gay Lussac* has shown, in the formation of two compounds which are gaseous at the ordinary temperature,  $\text{NOCl}_2$  (chloronitric acid), and  $\text{NOCl}$  (chloronitrous gas), and of Cl and water. If one equivalent of  $\text{HNO}_3$  is used to three equivalents of  $\text{HCl}$ , it may be assumed that only chloronitric acid ( $\text{NOCl}_2$ ), Cl and  $\text{H}_2\text{O}$  are formed ( $\text{HNO}_3 + 3\text{HCl} = \text{NOCl}_2 + \text{Cl} + 2\text{H}_2\text{O}$ ). This decomposition ceases as soon as the fluid is saturated with the gas; but it recommences the instant

this state of saturation is disturbed by the application of heat or by decomposition of the acid. The presence of the Cl, and also, but in a very subordinate degree, that of the acids named, makes aqua regia the most powerful solvent for the metals, with the exception of those which form insoluble chlorides."

This test is employed in an undiluted state.

4.  $\text{H}_2\text{SO}_4$ , *Sulphuric acid* (oil of vitriol), frequently contains As, Pb,  $\text{Fe}'''$ , Ca, and oxides of nitrogen. The Pb is deposited to a great extent when the acid is diluted  $\text{PbSO}_4$ , being less soluble in dilute than in concentrated  $\text{H}_2\text{SO}_4$ .

This acid ought to leave no residue upon evaporation on platinum; and if it does not remain perfectly clear upon dilution with four or five parts of spirits of wine,  $\text{PbSO}_4$ ,  $\text{Fe}_2'''3\text{SO}_4$ , or  $\text{CaSO}_4$  is present. "The presence of small quantities of Pb is detected most easily by adding some HCl to the  $\text{H}_2\text{SO}_4$  in a test-tube; if the point of contact is marked by turbidity ( $\text{PbCl}_2$ ), Pb is present." If a solution of  $\text{FeSO}_4$  is poured upon some of the acid in a test-tube, so that the iron solution floats upon the acid, a purplish red ring will be formed at the junction of the two solutions, if the acid contains nitric or hyponitric acid. If, after dilution with 20 parts of water, it imparts a blue tint to a solution of KI, mixed with starch paste, hyponitric acid is present. Examine it for arsenic by Marsh's test, described in the fifth group of bases.

Fresenius recommends the following process for the preparation of pure sulphuric acid: Take of strong sulphuric acid 1000 grm., ammonic sulphate 3 grm., manganic peroxide in powder 5 grm., put the acid in a porcelain dish, add the ammonic sulphate, and heat till copious fumes of  $\text{H}_2\text{SO}_4$  escape; this is done to destroy any oxides of nitrogen. After cooling, add the manganic peroxide, and heat to boiling, with stirring, in order to convert any arsenious into arsenic acid. When cool, pour off the clear fluid into a retort about a litre in capacity, and distil. The neck of the retort must reach so far into the receiver that the distillate may drop directly into its body. The receiver should not be cooled with water. To prevent the neck of the retort from touching the receiver, some long asbestos may be used. When about 10 c. c. have been drawn over, change the receiver, and distil off three-fourths of the contents of the retort. This method depends upon the fact that sul-

phuric acid containing arsenic in the form of arsenic acid, yields an arsenic-free distillate.

The dilute acid is prepared by adding four parts of water to every one of the concentrated acid.

5.  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6\text{H}_2\text{T}$ , *Tartaric acid* is generally sufficiently pure for analytical purposes. As it undergoes decomposition in solution, a small quantity only should be prepared at a time.

For use, dissolve one part, by weight, of acid, in two parts, by measure, of water.

6.  $\text{NaHC}_4\text{H}_4\text{O}_6$ , *Sodic hydric tartrate* is prepared by dissolving a quantity of tartaric acid in water, dividing the solution into two equal parts, and neutralizing one exactly with  $\text{Na}_2\text{CO}_3$ , and then adding the other portion, and afterwards evaporating the whole solution until the bitartrate crystallizes.

For use, make a saturated solution.

7.  $\text{HC}_2\text{H}_3\text{O}_2 = \text{H}\bar{\text{A}}$ , *Acetic acid*, when employed in analysis, ought to leave no residue on evaporation, and after saturation with  $\text{Na}_2\text{CO}_3$ , emit no empyreumatic odor. It ought to give no precipitate with  $\text{BaCl}_2$  and  $\text{AgNO}_3$ , and it ought to give no color or turbidness with  $\text{H}_2\text{S}$ , or with  $(\text{NH}_4)_2\text{S}$ , after it has been neutralized with  $\text{NH}_4\text{HO}$ .

The ordinary commercial acetic acid is sufficiently concentrated for analytical purposes.

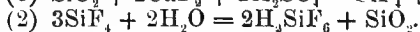
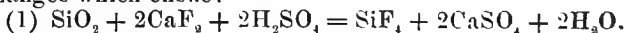
8.  $\text{H}_2\text{S}$ , *Hydrosulphuric acid* (sulphuretted hydrogen) is prepared by adding to  $\text{FeS}$ , in an appropriate apparatus, dilute  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$ . The  $\text{H}_2\text{S}$  is liberated in its gaseous state, and may be passed through any solution under examination; or a solution of the gas may be obtained by passing it through pure water. As this solution very soon decomposes by contact with the atmosphere, it ought to be prepared very frequently, and kept in well-stoppered bottles.

$\text{FeS}$ , from which  $\text{H}_2\text{S}$  is obtained, is prepared by projecting a mixture of thirty parts of iron filings with twenty-one of flowers of sulphur, in small portions at a time, into a red-hot crucible, replacing the cover after each addition. When the whole has been added, the ignition must be continued for a short time, until the excess of sulphur has been dissipated. Bloxam has found that  $\text{H}_2\text{S}$ , prepared from  $\text{FeS}$ , contains arsenic, but if obtained from native sulphide of antimony and  $\text{HCl}$  it is free from it; it ought, in examination for poisons at least, always to be prepared from the antimony sulphide.

9.  $\text{SO}_2$ , *Sulphurous anhydride*, is prepared by acting upon copper or charcoal with sulphuric acid. For this purpose small pieces of charcoal are introduced into a flask, with from six to eight times their weight of  $\text{H}_2\text{SO}_4$ , and a moderate heat applied. The evolved gas must be conducted into cold water until it is no longer absorbed. On account of the great tendency which this reagent has to absorb more oxygen, and become converted into  $\text{H}_2\text{SO}_4$ , it must be preserved in well-stoppered bottles.

10.  $\text{Cl}$ , *Chlorine gas*, is prepared by mixing 18 parts of  $\text{NaCl}$  with 15 parts of finely powdered  $\text{MnO}_2$ ; the mixture is placed in a flask and upon it is poured a *completely cooled* mixture of 45 parts of concentrated  $\text{H}_2\text{SO}_4$ , and 21 parts of water, the flask is then shaken. A uniform and continuous evolution of  $\text{Cl}$  will soon begin, which, when slackening, may be easily increased again by the application of a *gentle* heat. A solution of the gas may be prepared by passing it into cold water. Chlorine water must be kept in well-stoppered bottles, and excluded from the light; for if exposed to light it is speedily converted into  $\text{HCl}$ , oxygen being evolved; when it has lost its odor it is unfit for use.

11.  $\text{H}_2\text{SiF}_6$ , *Hydrofluosilicic acid*. This acid is prepared as follows: Take 1 part of sand, wash it and dry it thoroughly, mix it with 1 part of calcic fluoride, also dry and place the mixture in a flask; 6 parts of concentrated  $\text{H}_2\text{SO}_4$  are then added. The mixture must only fill the flask one-third, as it swells up on being warmed; heat the flask by means of a sand-bath; a gas delivery tube dips into a vessel containing 4 parts of water and some mercury; the tube dips beneath the surface of the mercury, to prevent the tube from being stopped up by the silica which is formed when the silicic fluoride ( $\text{SiF}_4$ ) comes in contact with water; the following diagrams express the chemical changes which ensue:—



12.  $\text{H}_2\text{C}_2\text{O}_4 = \text{H}_2\text{O}$ , *Oxalic acid*. Dissolve one part, by weight, of the acid, in twenty parts, by measure, of water.

13.  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ , *Ammonic oxalate*, ought to leave no residue after ignition on platinum foil, and it ought not to give a precipitate, nor be rendered turbid, by  $\text{H}_2\text{S}$  nor by  $(\text{NH}_4)_2\text{S}$ .

Dissolve one part, by weight, of the salt, in twenty-four parts, by measure, of water.

14.  $\text{NH}_4\text{HO}$ , *Ammonia*, must be colorless, and leave no

residue upon evaporation to dryness. It ought not, after being diluted with three volumes of distilled water, to give a precipitate on the addition of lime-water. It ought not, after being acidulated with pure  $\text{HNO}_3$ , to give a precipitate with  $\text{Ba}(\text{NO}_3)_2$  nor with  $\text{AgNO}_3$ .  $\text{H}_2\text{S}$  ought not to impart to it the slightest color, and on the addition to it of a few drops of a solution of ammonio-sulphate of copper, a black precipitate ought not to be formed.

15.  $\text{NH}_4\text{Cl}$ , *Ammonic chloride*.—This salt ought to volatilize completely when ignited on platinum foil; the solution ought to be neutral to test-paper, and it ought to give no precipitate nor coloration on the addition of  $(\text{NH}_4)_2\text{S}$ .

Dissolve one part, by weight, of the salt, in eight parts, by measure, of water.

16.  $(\text{NH}_4)_2\text{S}$ , *Ammonic sulphide*, is prepared by passing hydrosulphuric acid through  $\text{NH}_4\text{HO}$ , until it does not produce a precipitate in a solution of  $\text{MgSO}_4$ . It ought not to produce a precipitate with a solution of lime, and it ought to leave no residue on evaporation to dryness and ignition.

17. *Ammonic carbonate* must completely volatilize. Its solution ought to give no precipitate or coloration with  $(\text{NH}_4)_2\text{S}$  nor with  $\text{H}_2\text{S}$  after acidulation with  $\text{HCl}$ . Its solution, after being acidulated with  $\text{HNO}_3$ , ought to produce no precipitate with  $\text{Ba}(\text{NO}_3)_2$  nor with  $\text{AgNO}_3$ .

Dissolve one part, by weight, of the salt, in four parts, by measure, of water, and add one measure of ammonia.

18.  $\text{NH}_4\text{NO}_3$ , *Ammonic nitrate*, is made by neutralizing  $\text{HNO}_3$  with  $(\text{NH}_4)_2\text{CO}_3$ . The solution is evaporated until crystals begin to be deposited, and is then allowed to cool; the crystals are afterwards fused.

19. *Ammonic arseniate* is prepared by neutralizing arsenic acid with ammonic carbonate and evaporating to dryness.

Dissolve one part, by weight, of the salt, in ten parts, by measure, of water.

*Arsenic acid* is prepared by dissolving arsenious acid in  $\text{HNO}_3$ , mixed with a little  $\text{HCl}$ , evaporating the solution to dryness, and igniting somewhat below a low red heat until all  $\text{HNO}_3$  is expelled.

20. *Ammonic molybdate in nitric acid*.—Dissolve one part of molybdic trioxide in eight parts of strong  $\text{NH}_4\text{HO}$ , or one part of acid ammonic molybdate in three parts of  $\text{NH}_4\text{HO}$ , with the aid of heat; pour the solution into twenty parts of  $\text{HNO}_3$ , consisting of equal parts of strong  $\text{HNO}_3$  and water.

21.  $K_2SO_4$ , *Potassic sulphate*.—Recrystallize the  $K_2SO_4$  of commerce; dissolve one part, by weight, of the purified salt in 200 parts, by measure, of water.

22.  $KNO_2$ , *Potassic nitrite*, may be prepared "by heating in a flask only half filled with the mixture two parts of starch, in pieces, with eight parts of impure  $HNO_3$  of 1.4 sp. gr. and eight parts of water, and conduct the nitrous fumes\* evolved first through a large empty flask, then into a flask containing a solution of KHO until it is completely saturated. If the potassic solution contains silicic acid or alumina, as is mostly the case, the saturation point is marked by the separation of these impurities. Five parts of solution of KHO of 1.27 sp. gr. is the quantity required in the process. As soon as the action begins, the flame under the evolution flask must be temporarily removed, or otherwise the action might become too energetic. Evaporate the filtered solution to dryness. Dissolve one part of the dry salt to about two parts of water when the reagent is required for use."

23.  $K_4FeCy_6$ , *Potassic ferrocyanide* (yellow prussiate of potash), is prepared on the manufacturing scale by adding animal matter, such as horns, feathers, dried blood, leather-clippings, etc., mixed with iron filings, to fused  $K_2CO_3$ , lixiviating the fused mass with water, then filtering and crystallizing by evaporation. The animal matter contains nitrogen and carbon, the latter in larger proportion than is required to form cyanogen with the nitrogen; hence when these substances are fused with  $K_2CO_3$ , the excess of carbon reduces the  $K_2CO_3$ ; the K being set free, unites with the cyanogen formed from the N and the remainder of the C producing KCN, which is converted into the ferrocyanide by the action of the KCN on the Fe when the fused mass is heated with water.

The commercial  $K_4FeCy_6$  is sufficiently pure for analytical purposes; dissolve one part by weight, in twelve, by measure, of water.

24.  $K_6Fe_2Cy_{12}$ , *Potassic ferricyanide* (red prussiate of potash), is prepared by the action of oxidizing agents on the ferrocyanide. It is usually prepared by passing washed chlorine gas (with constant agitation to insure uniformity of action) through a cold solution of the ferrocyanide until it no longer gives a blue but a brown color with a ferric salt.

\* Nitrous anhydride ( $N_2O_3$ ) nearly in a state of purity.

Dissolve one part, by weight, in twelve, by measure, of water; the solution ought to be made as it is wanted, as ferricyanide decomposes when in a state of solution, a trace of ferrocyanide being formed.

25.  $\text{NH}_4\text{CyS}$ , *Ammonic sulphocyanide*;  $\text{KCyS}$ , *Potassic sulphocyanide*.— $\text{NH}_4\text{CyS}$  may be prepared (1) by digesting  $\text{HCy}$  with ammonic polysulphide, prepared by digesting sulphur in  $(\text{NH}_4)_2\text{S}$ , taking care to keep the latter slightly in excess, which is indicated by the yellow color of the solution, then boiling off the excess of the latter, filtering and evaporating to the crystallizing point:  $2\text{CNH} + (\text{NH}_4)_2\text{S}_2 = 2\text{NH}_4\text{CyS} + \text{H}_2\text{S}$ . (2) A mixture of 750 parts of  $\text{NH}_4\text{HO}$  and 100 parts of  $\text{CS}_2$  (carbonic disulphide), and 750 parts of alcohol, 86 per cent., is distilled down to one-half after standing for 24 hours, the residual liquid is evaporated to the crystallizing point:  $4\text{NH}_4\text{HO} + \text{CS}_2 = \text{NH}_4\text{CyS} + (\text{NH}_4)_2\text{S} + 4\text{H}_2\text{O}$ . Potassic sulphocyanide may be prepared by heating to low redness in a covered vessel a mixture of 46 parts of dried  $\text{K}_4\text{FeCy}_6$ , 37 parts of  $\text{S}$ , and 17 parts of pure  $\text{K}_2\text{CO}_3$ ; the mass after heating is exhausted with water; the watery solution is evaporated to dryness on the water-bath, and the residue is exhausted with alcohol, which deposits crystals on cooling or evaporation.

Dissolve 1 part, by weight, of either salt in 10 parts of water.

26.  $\text{K}_2\text{CrO}_4$ , *Potassic chromate*, in solution ought not, after it has been acidulated with  $\text{HCl}$ , to give a precipitate with  $\text{BaCl}_2$ .

Dissolve 1 part, by weight, in 8 parts, by measure, of water.

27.  $\text{KCN} = \text{KCy}$ , *Potassic cyanide*, is prepared by mixing intimately 8 parts of *anhydrous* potassic ferrocyanide and 3 parts of potassic carbonate, and introducing the mixture by small portions into a cast-iron crucible previously heated to low redness; after all the materials have been added, the crucible is kept in the fire till a sample of the fused mass taken out on a glass rod appears white, and exhibits the aspect of porcelain on cooling; the crucible is then removed from the fire and left at rest for a moment to allow the iron liberated by the decomposition to settle down; it is then poured out carefully, to prevent the running out of the minute particles of iron, into a clean iron or silver vessel. Thus prepared, it always contains a little

potassic carbonate and cyanate. The potassic carbonate employed must be free from sulphate, as this would be reduced to sulphide by the cyanide. It may also be prepared by igniting the ferrocyanide *alone*; but as one-third of the cyanogen in this case is resolved into carbon and nitrogen, only two-thirds is obtained in the form of the salt.

28.  $\text{NaHO}$ , *Sodic hydrate* (caustic soda), is prepared by dissolving 1 part, by weight, of  $\text{Na}_2\text{CO}_3$ , in 9 parts, by measure, of water, and boiling the solution in a clean iron pan; milk of lime, prepared by adding 1 part of  $\text{CaO}$  (quicklime) to 3 parts of boiling water, is then added in small portions to the boiling liquid, until  $\text{HCl}$  causes no effervescence in a portion of the clear liquid. When this point has been attained, the pan must be removed from the fire, and the precipitate allowed to subside. The supernatant liquid must then be drawn off by means of a syphon, or passed through a filter of bleached linen, and the filtrate evaporated rapidly over a quick fire until it has been reduced to half its original bulk. On supersaturating a portion of the liquid with  $\text{HCl}$ , no, or only a slight, effervescence should take place.  $\text{H}_2\text{S}$  must not produce a precipitate or coloration in its solution. The solution must be evaporated until it has a sp. gr. of from 1.13 to 1.15; it must be kept in well-stoppered bottles.

29.  $\text{Na}_2\text{CO}_3$ , *Sodic carbonate*, in solution ought not, after it has been acidulated with  $\text{HNO}_3$ , to give a precipitate with  $\text{BaCl}_2$  nor with  $\text{AgNO}_3$ .

Dissolve 1 part, by weight, of the salt, in 10 parts, by measure, of water.

30.  $\text{Na}_2\text{HPO}_4$ , *Disodic hydric phosphate*, must form no precipitate with ammonia.

Dissolve 1 part, by weight, of the salt, in 10 parts, by measure, of water.

31.  $\text{NaC}_2\text{H}_3\text{O}_2$ , *Sodic acetate*, is made by adding acetic acid to a concentrated solution of  $\text{Na}_2\text{CO}_3$  until all effervescence ceases. This solution must be free from sulphates.

Dilute 1 part of the concentrated solution with 4 parts of water.

32.  $\text{NaHSO}_3$ , *Sodic hydric sulphite*.—Pass  $\text{SO}_2$ , prepared as directed at 9, page 376, through a bottle containing a small quantity of water, then into a flask containing a solution of  $\text{Na}_2\text{CO}_3$  (prepared by dissolving 7 parts of the pure crystallized carbonate in from 20 to 30 parts of water) until  $\text{CO}_2$  ceases to be evolved. The solution must be



kept in a well-stoppered bottle, as it has a great tendency to absorb oxygen, and pass from sulphite to sulphate.

33.  $\text{Na}_2\text{B}_4\text{O}_7(\text{H}_2\text{O})_{10}$ , *Borax*, is employed in blowpipe analysis. It should be heated below the fusing point to drive off its water of crystallization, and then powdered.

34. *Sodic and Potassic carbonate*.—Equal parts of these two carbonates in the anhydrous state must be mixed together. They must not contain any sulphate.

35.  $\text{NaNH}_2\text{HPO}_3$ , *Sodic ammoniac hydric phosphate* (microcosmic salt). This salt, which is found in human urine after putrefaction, and in guano from Ichaboe, may be prepared artificially in several ways; the following is a very convenient method: .6 or 7 parts of crystallized disodic hydric phosphate ( $\text{Na}_2\text{HPO}_4$ ) and 1 part of  $\text{NH}_4\text{Cl}$  are dissolved in 2 parts of boiling water, the  $\text{NaNH}_2\text{HPO}_3$  crystallizes out as the solution cools, the  $\text{NaCl}$  remaining in solution; the phosphate may be freed from  $\text{NaCl}$  by recrystallization from a small quantity of boiling water containing a little  $\text{NH}_4\text{HO}$ .

36.  $\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7$ , *Dihydric dipotassic metantimoniate*, may be prepared by projecting a mixture of equal parts of powdered tartar emetic and potassic nitrate in small portions at a time into a red-hot crucible. After the mass is deflagrated keep it at a moderate heat for a quarter of an hour longer, then remove it from the fire, and when sufficiently cold treat it with warm water; transfer the mixture to a suitable vessel, and decant the *clear* fluid from the heavy powder and concentrate it. After one or two days a doughy mass will separate from the liquid; treat this mass with three times its volume of cold water, working it at the same time with a spatula. This operation will serve to convert it into a fine granular powder, to which add the powder from which the fluid was decanted, wash slightly, and dry on blotting-paper. Prepare the solution only immediately before it is required for use, by shaking the salt with cold water, and filtering off the fluid from the undissolved portion; it must be clear, and of neutral reaction; it must give no precipitate with solution of  $\text{KCl}$ , or with one of  $\text{NH}_4\text{Cl}$ , but must produce a crystalline precipitate with one of  $\text{NaCl}$ .

37.  $\text{BaCl}_2$ , *Baric chloride*.—A solution of this salt must be neutral to test-paper; after precipitation by  $\text{H}_2\text{SO}_4$  the filtrate ought not to leave the slightest residue when evaporated on platinum foil. Its solution ought not to

give a precipitate or be colored by the addition of  $\text{H}_2\text{S}$  or by  $(\text{NH}_4)_2\text{S}$ .

Dissolve 1 part of the salt in 10 of water.

38.  $\text{Ba}(\text{NO}_3)_2$ , *Baric nitrate*.—A solution of this salt must not be rendered turbid by  $\text{AgNO}_3$ ; for other impurities, test as directed in  $\text{BaCl}_2$ .

Dissolve 1 part of the salt in 10 parts of water.

39. *Lime-water* is made by digesting recently prepared  $\text{CaH}_2\text{O}_2$  for some time with cold distilled water, with frequent agitation of the mixture; allow the undissolved portion of the lime to subside, decant subsequently, and keep the clear fluid in well-stoppered bottles.

40.  $\text{CaCl}_2$ , *Calcic chloride*, is made by dissolving pure  $\text{CaCO}_3$  in dilute  $\text{HCl}$ ; the solution thus obtained must be neutral to test-paper, and it must not form a precipitate, nor be colored by  $(\text{NH}_4)_2\text{S}$ .

41.  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , *Calcic sulphate* (gypsum).—Dissolve as much of the salt as the water will take up.

42.  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , *Magnesian sulphate* (Epsom salts).—Dissolve 1 part in 8 of water.

43.  $\text{BaCO}_3$ , *Baric carbonate*, may be prepared by dissolving  $\text{BaCl}_2$  in hot water, and precipitating by  $(\text{NH}_4)_2\text{CO}_3$  and  $\text{NH}_4\text{HO}$ ; the precipitate must be washed until the last washing gives no turbidness with  $\text{AgNO}_3$ . Stir the precipitate with water to the consistence of cream, and keep the mixture in a stoppered bottle; shake the mixture before using it.

44.  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , *Ferrous sulphate*.—The purified commercial salt is sufficiently pure; it is principally employed for the detection of nitric acid.

Dilute 1 part of the concentrated solution with 3 parts of water.

45.  $\text{Fe}_2\text{Cl}_6$ , *Ferric chloride*, is prepared by dissolving recently precipitated and well-washed  $\text{Fe}_2\text{H}_6\text{O}_6$  in pure  $\text{HCl}$ ; the ferric hydrate must be kept during the solution slightly in excess, as the ferric chloride must contain no free acid; it is afterwards diluted with an equal volume of water and filtered.

46.  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , *Plumbic acetate*.—The best commercial acetate is sufficiently pure to be used as a reagent; dissolve 1 part, by weight, of the salt, in 10 parts, by measure, of water.

47.  $\text{HgNO}_3$ , *Mercurous nitrate*, is made by gently heating in a small flask 9 parts of  $\text{HNO}_3$ , in conjunction with 10 parts of  $\text{Hg}$ , until the disengagement of nitrous fumes

ceases; the solution is then boiled for some time with the undissolved portion of the Hg, care being taken to replace the water lost by evaporation. The crystals, which separate on the cooling of the liquid are dissolved in 20 parts of cold water, slightly acidulated with  $\text{HNO}_3$ . The fluid is then filtered if necessary, and the filtrate kept in a glass bottle, the bottom of which is covered with mercury.

48.  $\text{HgCl}_2$ , *Mercuric chloride*.—Dissolve 1 part of the salt in 16 parts of water.

49.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , *Cupric sulphate*.—The commercial salt is purified by two or three crystallizations; dissolve 1 part, by weight, of the purified crystals, in 10 parts, by measure, of water.

50. *Ammonio-sulphate of copper* is prepared by adding  $\text{NH}_4\text{HO}$ , drop by drop, to a not too concentrated solution of  $\text{CuSO}_4$ , until the precipitate at first produced is nearly redissolved; the clear solution to be employed.

51.  $\text{AgNO}_3$ , *Argentive nitrate*, is prepared by dissolving pure Ag in pure  $\text{HNO}_3$  diluted with an equal bulk of water, evaporating the solution to dryness and gently fusing the residue; if pure, its solution will, after addition of  $\text{HCl}$  in excess and filtering, leave no fixed residue. Dissolve 1 part, by weight, of the salt, in 20 parts, by measure, of water.\*

52. *Ammonio-nitrate of silver* is prepared by adding  $\text{NH}_4\text{HO}$ , drop by drop, to a solution of  $\text{AgNO}_3$ , until the precipitate at first formed is nearly redissolved; the clear solution to be employed.

53.  $\text{Co}(\text{NO}_3)_2$ , *Cobaltic nitrate*.—This salt can be purchased fit for use; dissolve 1 part, by weight, in 10 parts, by measure, of water.

54.  $\text{PtCl}_4$ , *Platinic chloride*.—Purify platinum scraps by boiling them in  $\text{HNO}_3$ ; when purified treat with concentrated  $\text{HCl}$ , and some  $\text{HNO}_3$ , in a narrow-necked flask and apply heat, add occasionally  $\text{HNO}_3$  until the Pt is dissolved. Evaporate the solution on the water-bath, to dryness, adding during the evaporation  $\text{HCl}$ , dissolve the residue in 10 parts of water. Dry  $\text{PtCl}_4$ , if pure, dissolves completely in spirits of wine.†

55.  $\text{AuCl}_3$ , *Auric chloride*.—If the gold is perfectly pure it has simply to be dissolved in aqua regia, and evaporated to dryness over the water-bath, and the residue redissolved in water. If it contains silver, filter off from the insoluble  $\text{AgCl}$ , which will remain on treating the residue with water.

\* See Appendix A, page 387.

† See Appendix B, page 388.

If it contains copper, which may be ascertained by diluting a portion of the acid solution, and adding to it  $K_4Fe_2Cy_{12}$ , mix it with a solution of  $FeSO_4$  in excess; collect the metallic gold, wash it, and then redissolve in aqua regia, and evaporate as before.\*

56.  $SnCl_2$ , *Stannous chloride*.—Boil granulated tin in concentrated  $HCl$  in a flask, keeping the tin always in excess until  $H$  ceases to be evolved, then dilute the solution with four times its volume of water containing a little  $HCl$ , and filter. Keep the filtrate in a well-stoppered bottle containing some fragments of tin.

57.  $PbO_2$ , *Plumbic peroxide*, may be prepared by digesting in boiling  $HNO_3$ , diluted with four or five times its bulk of water, red lead in fine powder; the residue is washed with a fresh quantity of the dilute  $HNO_3$ , and then with water until everything soluble is removed.

58. *Copper turnings* are employed for the detection of nitric acid.

59. *Zinc* must be perfectly free from arsenic. Test for this impurity as directed at par. 262.

60. *Nessler's test*.—"This reagent is an aqueous solution of potassic iodide, saturated with mercuric iodide, and rendered powerfully alkaline with soda or potash. It is prepared by dissolving 50 grammes of  $KI$  in a small quantity of hot distilled water. The vessel containing this solution is placed on the water-bath, and to it is added a strong solution of  $HgCl_2$ , which will cause a red precipitate ( $HgI_2$ ), that disappears on shaking the mixture. The  $HgCl_2$  solution is carefully added, the liquid being at the same time shaken, so as to dissolve the precipitate as fast as it is formed; the addition of the  $HgCl_2$  solution is continued until the precipitate ceases to be dissolved. When this point is reached no more  $HgCl_2$  must be added. The mixture is then filtered, and to the filtrate is added 150 grammes of solid  $NaHO$  in strong aqueous solution (or about 200 grammes of solid  $KHO$  dissolved in water). After the addition of the alkali solution, the liquid is diluted so as to make its volume equal to one litre. Add to the diluted liquid about 5 cub. cent. of a saturated aqueous solution of  $HgCl_2$ ; allow to subside, and decant the clear liquid.

"As exposure to the air is apt to render this reagent somewhat turbid, it is advisable to keep the stock of the reagent in a large bottle, which should only be opened to supply a small bottle kept to hold that which is in imme-

\* See Appendix C, page 389.

ciate use. The addition of the 5 c. c. of solution  $\text{HgCl}_2$  has two objects; it causes the reagent to clear rapidly, and imparts sensitiveness to the reagent when deficient in that quality." (Wanklyn and Chapman on Water Analysis.)

61. *Solution of indigo*.—"Take from 4 to 6 parts of fuming  $\text{H}_2\text{SO}_4$ , add slowly and in small portions at a time 1 part of finely pulverized indigo, taking care to keep the mixture well stirred. The acid has at first imparted to it a brownish tint by the matter which the indigo contains in admixture, but it subsequently turns blue. Elevation of temperature to any considerable extent must be avoided, as part of the indigo blue is thereby destroyed; it is therefore advisable, when dissolving larger quantities of the substance, to place the vessel in cold water. When the whole of the indigo has been added to the acid, cover the vessel, let it stand forty-eight hours, then pour its contents into twenty times the quantity of water, mix, filter, and keep the filtrate for use."

62. *Distilled water* ought always to be employed in all the above solutions and in all analytical operations. It should leave no residue on evaporation, and should give no precipitate or even turbidity, with  $\text{BaCl}_2$ ,  $\text{AgNO}_3$ ,  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ , or lime-water.

63. *Reagent papers*.—Blue litmus paper serves to detect the presence of free acids or of acid salts in fluids, since they change the blue color to red. Reddened litmus paper serves to detect the presence of free alkalies, and of earths and salts possessing an alkaline reaction, by changing the red color to blue. Turmeric paper aids, like reddened litmus paper, in the detection of free alkalies, etc., by changing its yellow color to brown.

*Preparation of blue litmus paper*.—"Digest 1 part of litmus of commerce with 6 parts of water, and filter the solution; divide the intensely blue filtrate into 2 equal parts; saturate the free alkali in the one part, by repeatedly stirring with a glass rod dipped in very dilute  $\text{H}_2\text{SO}_4$ , until the color of the fluid just appears red; add now the other part of the blue filtrate, pour the whole fluid into a dish, and draw strips of fine, unsized paper through it; suspend these strips over threads, and leave them to dry. The color of litmus paper must be perfectly uniform, and neither too light nor too dark."

*Preparation of reddened litmus paper*.—"Stir blue solution of litmus with a glass rod dipped in dilute  $\text{H}_2\text{SO}_4$ , and repeat this process until the fluid has just turned distinctly

red. Steep slips of paper in the solution, and dry them as directed in the preceding paragraph. The dried slips must look distinctly red."

Vacher prepares a paper of neutral tint thus: Digest 20 grm. litmus with 100 c. c. water for some days, shaking occasionally, then filter. To the filtrate add slight excess of  $\text{HNO}_3$  and boil; then neutralize exactly with  $\text{KHO}$ . Now make a weak solution of gelatine by boiling 1 part of isinglass with 50 parts of water; draw white blotting-paper through this, and hang it up to dry. When dry, paint one side with the above solution.

*Preparation of turmeric paper.*—Digest and heat 1 part of bruised turmeric root with 6 parts of weak spirit of wine, filter the tincture obtained, and steep slips of fine paper in the filtrate. The dried slips must exhibit a fine yellow tint.

*Schonbein's test-papers for hydrocyanic acid.*—Three parts of resin of guaiacum are dissolved in 100 parts of rectified spirit; white filtering paper is steeped in this solution and dried. The paper should remain white. The solution of cupric sulphate, with which these papers are to be moistened just before being used, is prepared by dissolving one part of cupric sulphate in 500 parts of water.

*Brazil-wood paper* is prepared by moistening slips of fine writing paper with decoction of Brazil wood.

#### APPARATUS.

1179. The processes employed in qualitative analysis are exceedingly simple, and do not require much apparatus for their execution. The small amount actually requisite is described in the following list, and may be procured in the shops of operative chemists.

1½ dozen test-tubes.	Small retort stand.
Test-tube stand.	3 small glass funnels.
2 small evaporating dishes.	2 porcelain crucibles.
Washing bottle.	½ lb. glass tubing.
Spirit lamp.	¼ lb. glass rod.
2 watch-glasses.	Small mortar and pestle.
Rat-tail and triangular file.	1 quire filtering paper.
Platinum wire and foil.	Crucible tongs.
Sulphuretted hydrogen apparatus.	Black's blowpipe.
A number of best corks.	Tube cleaner.
A few lengths of small vulcanized tubing.	Small German beakers.
	Litmus paper, blue and red.
	Turmeric paper.

## APPENDICES.

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APPENDIX A. TREATMENT OF SILVER RESIDUES.—Waste solutions containing silver must not be poured into the sink, but into a bottle containing some commercial hydrochloric acid; when a quantity of the precipitated  $\text{AgCl}$  has collected sufficient, in the opinion of the experimentalist, for reduction, it may be thrown upon a filter, washed thoroughly with hot water and afterwards dried; when dry it must be detached from the filter, and the filter must then be burnt until all the carbonaceous matter of the filter is destroyed; the filter ash along with the silver it may contain may be added to the silver salt or placed in the silver residue bottle. The silver may be obtained from the dried  $\text{AgCl}$  by one or other of the following processes: (1) Mix it with twice its weight of reagent 34 (page 381), and then introduce the mixture into a Cornish clay crucible which it ought only to half fill, and afterwards place the crucible in a furnace and raise the heat gradually until the mixture becomes fluid, keep it in that state for about five minutes, and then remove the crucible from the furnace, tap it slightly on the bottom two or three times so as to cause all the particles of silver to collect together in a mass, and then allow it to cool; when cold, the crucible is broken and the silver, which has collected in the form of a button if the operation has been well performed, is removed and freed by washing from any adherent particles of the alkaline salts. This process succeeds with experienced chemists, but often fails with beginners, for the heat must be gradually applied and the crucible not more than half full, otherwise the effervescence caused by the evolution of  $\text{CO}_2$  and  $\text{O}$  may cause a loss of the substance; and the heat finally must be high enough, otherwise the silver remains disseminated through the mass of the alkaline salts; and yet it must not be too high, otherwise the crucible is corroded and the silver flows into the fire. In order to obviate these

disadvantages, the late Professor Gregory recommended the *undried* AgCl to be boiled with a very strong solution of caustic potash, till it is entirely or in great part converted into black oxide of silver; this is then collected, washed thoroughly, then dried, and, finally, fused with a little potassic carbonate and borax, which yields a button of silver without any risk. If all the AgCl was converted into Ag<sub>2</sub>O by boiling with KHO, simple ignition would be sufficient to obtain the silver in the metallic state. (2) Boil 6 parts of silver chloride for half an hour with 9 parts of a solution of caustic soda of 1.333 sp. gr., 1½ parts of clarified honey, and 8 parts of water; when the heat is withdrawn let the finely divided silver collect at the bottom of the vessel, and then pour off the liquid and wash the silver thoroughly by decantation. (3) The AgCl is placed in contact with iron or zinc and water, to which, in order to accelerate the action, a small quantity of HCl or H<sub>2</sub>SO<sub>4</sub> may be added; the reduced silver must be quickly washed first with acidulated and afterwards with hot pure water, and then fused with borax and nitre. Convert the metallic silver obtained by any of these different processes into nitrate as directed at 51 (page 383).

#### APPENDIX B. TREATMENT OF PLATINUM RESIDUES.—

Platinum residues are collected in a bottle, and when a sufficient quantity has collected the mixture, the liquid and precipitate, is evaporated to dryness in a porcelain dish, and ignited so as to decompose the platinic salts, and the residue washed to remove the soluble matter; a small quantity of oxalic acid in solution is then added to it, and the mixture is again evaporated and ignited so as to decompose any PtCl<sub>4</sub>, 2KCl, which may have escaped decomposition on the first ignition; the ignited mass is again thoroughly washed with hot water, it must then be boiled in dilute HCl and the insoluble portion again washed thoroughly with hot water; it is then converted into PtCl<sub>4</sub>, as directed at 54 (page 383). If the dry PtCl<sub>4</sub> does not dissolve completely in spirits of wine it must be redissolved in water, and a saturated solution of NH<sub>4</sub>Cl added to it, the precipitated PtCl<sub>4</sub>, 2NH<sub>4</sub>Cl must be collected upon a filter, washed first with a little water, and finally with methylated spirit and ignited; the spongy platinum thus obtained must be converted into PtCl<sub>4</sub>, as directed at 54 (page 383).



APPENDIX C. TREATMENT OF GOLD RESIDUES.—Gold residues are collected in a bottle, and when a sufficient quantity has collected the mixture is evaporated to dryness and ignited. The ignited mass is washed thoroughly with hot water, and the insoluble matter is dissolved in aqua regia; evaporate to dryness over the water-bath; redissolve the residue in water; mix it with an excess of saturated solution of oxalic acid and boil for some time; finally, free by washing the spongy mass of gold from foreign matter, and then convert it into  $\text{AuCl}_3$ , as directed at 55 (page 383).



# INDEX.

- ACETATES**, properties of, 224  
 Acetic acid as reagent, 375  
   behavior of, with reagents, 224  
   detection of, 230  
   properties of, 224  
**Acids**, classification of, 175  
   organic, classification of, 228  
   of the bile in calculi, 318  
   volatile inorganic, behavior of salts  
     of, with sulphuric acid, 214  
 Action of water on lead, 154  
**Albumen**, behavior of, with reagents, 283  
   composition of, 280  
   detection of, 289  
   examination for, 310  
   properties of, 278, 320  
   varieties of, 285  
**Albuminoids**, Gerhardt's views on the  
   constitution of, 281  
   Mulder's views on the constitution  
     of, 281  
   Strecker's views on the constitution  
     of, 282  
**Albuminoid substances**, 278  
**Alcohol**, conversion into acetic acid, 225  
**Alkaloids**, poisonous, detection of, in or-  
   ganic mixtures, 311  
**Aluminic chloride**, properties of, 82  
   compounds, blowpipe test for, 85  
   characteristic tests for, 85  
   properties of, 81  
   nitrate, properties of, 82  
   oxide, properties of, 80  
   phosphate, properties of, 90  
   sulphate, properties of, 82  
   sulphide, properties of, 81  
**Aluminium**, properties of, 79, 84  
**Ammonia** as reagent, 376  
   examination for, 35, 41  
   Nessler's test for, 42  
   properties of, 39  
**Ammonic arseniate** as reagent, 377  
   carbonate as reagent, 377  
   chloride as reagent, 377  
     properties of, 40  
   compounds, characteristic tests for,  
     42  
     properties of, 41  
     special tests for, 41  
   hydrate, properties of, 39  
   molybdate as reagent, 377  
   nitrate as reagent, 377  
   oxalate as reagent, 376  
   oxide, 33  
   sulphate, properties of, 40  
**Ammonic—**  
   sulphide as reagent, 377  
   sulphocyanide as reagent, 379  
   urate in calculi, 317  
**Ammonio-nitrate** of silver as reagent, 38  
   sulphate of copper as reagent, 383  
**Ammonium**, compounds of, 39, 41  
**Analysis** of animal secretions, 309  
   substances, 277  
   calculi, 317  
   ash of organic substances, 273  
   organic substances, 269  
   solids insoluble in acids, 262  
     soluble in acids, 262  
       in water, 261  
   urine, 277, 313  
   first basic group, 35  
     precautions, 36  
   second basic group, 47  
     Frobenius's method, 57  
     photo-chemical method, 58  
     precautions, 51  
   third basic group, 61  
     precautions, 64  
   fourth basic group, first method, 77  
     second method, 77  
     third method, 79  
     containing phosphates and  
       oxalates, 94  
   fifth basic group, first method, 99  
     second method, 100  
     third method, 100  
     fourth method, 101  
     fifth method, 101  
     sixth method, 101  
   sixth basic group, 136  
     precautions, 140  
   first group inorganic acids, 208  
   second group inorganic acids, 208  
   third group inorganic acids, 209  
   fourth group inorganic acids, 210  
   first group organic acids, 228  
   second group organic acids, 229  
   third group organic acids, 229  
   fourth group organic acids, 229  
**Animal secretions**, analysis of, 309  
   substances, behavior of, with rea-  
     gents, 279  
     distillation of, 278  
     oxidation of, 278  
     proximate analysis of, 277  
**Antimonious chloride**, properties of, 108  
   hydrate, properties of, 113  
   oxide, properties of, 104  
   salts, properties of, 112

**Antimonious—**

sulphide, properties of, 105

**Antimonuretted hydrogen, properties of, 111****Autimony compounds, blowpipe tests for, 118**

characteristic tests for, 118

flame reactions, 118

properties of, 118

special tests for, 118

detection of, in organic mixtures, 117

hydride of, properties of, 111

properties of, 102, 118

**Apparatus, list of, 388****Argentio chloride, properties of, 145**

compounds, blowpipe tests for, 147

characteristic tests for, 148

properties of, 146

nitrate as reagent, 483

properties of, 146

oxide, properties of, 143

peroxide, 148

salts, properties of, 148

suboxide, 148

sulphate, properties of, 146

sulphide, properties of, 144

**Arrangement of results, 30****Arsenates, behavior of, with reagents, 132**

properties of, 113

**Arsenic acid as reagent, 377**

behavior of, with reagents, 132

characteristic tests for, 211

properties of, 113

**Arsenic anhydride, properties of, 104**

compounds flame reactions, 131

properties of, 119

special tests for, 119

detection of, by electrolysis, 128

in organic mixtures, 128

dialytic method for detection of, 128

hydride of, properties of, 111

Marsh's test for, 122

precautions, 124

properties of, 102, 119

Reinsch's test for, 125

sulphide, properties of, 105

**Arsenious acid, characteristic tests for, 211**

properties of, 113

**Arsenious anhydride, properties of, 104**

chloride, properties of, 108

oxide, behavior of, with reagents, 119

sulphide, properties of, 105

**Arsenites, behavior of, with reagents, 120**

properties of, 113

**Arsenuretted hydrogen, properties of, 111**

Ash of organic substances, analysis of, 273

constituents of, 274

**Auric chloride as reagent, 383**

properties of, 110

compounds, properties of, 132

special tests for, 133

oxide, properties of, 104

salts, properties of, 118

sulphide, properties of, 105

**Aurous oxide, properties of, 133****Baric—**

compounds, special tests for, 55

characteristic tests for, 55

flame reactions, 55

properties of, 55

oxide, properties of, 51

nitrate as reagent, 382

properties of, 53

salts, general character of, 54

sulphate, properties of, 53

sulphide, properties of, 52

**Barium, properties of, 51, 55****Basic groups, behavior of, with reagents, 188**

list of, 29

**Bassorin, 324****Behavior of acetic acid with reagents, 224**

albumen with reagents, 283

animal substances with reagents, 279

arsenates with reagents, 132

arsenic acid with reagents, 132

arsenious oxide with reagents, 119

arsenites with reagents, 120

basic groups with group reagents, 166

benzoic acid with reagents, 222

bilirubine with reagents, 307

boracic acid with reagents, 180

brucine with reagents, 339

calculi on heating, 313

cane-sugar with reagents, 325

carbonic acid with reagents, 185

casein with reagents, 288

cellulose with reagents, 321

chloric acid with reagents, 206

cholepyrrhin with reagents, 307

cholestrin with reagents, 307

chondrin with reagents, 293

chromic acid with reagents, 176

cinchonine with reagents, 336

citric acid with reagents, 219

creatin with reagents, 301

creatinine with reagents, 300

cystine with reagents, 305

elements at high temperatures, 361

fibrin with reagents, 287

first basic group with special reagents, 34

formic acid with reagents, 226

fourth basic group with special reagents, 78

gallic acid with reagents, 224

gelatin with reagents, 292

glucose with reagents, 294

glutin with reagents, 292

glyco-cholinic acid with reagents, 304

grape sugar with reagents, 295

gum with reagents, 324

hippuric acid with reagents, 303

hydriodic acid with reagents, 196

hydrobromic acid with reagents, 198

hydrochloric acid with reagents, 194

hydrocyanic acid with reagents, 200

hydrofluoric acid with reagents, 191

hydrosulphuric acid with reagents, 193

hyposulphurous acid with reagents, 180

inosite with reagents, 297

iodic acid with reagents, 197

lactic acid with reagents, 302

lignin with reagents, 321

malic acid with reagents, 221

**BARIC carbonic as reagent, 382**

chloride as reagent, 381

properties of, 62

## Behavior of—

- meconic acid with reagents, 310
- metaphosphoric acid with reagents, 185
- milk sugar with reagents, 295
- morphine with reagents, 329
- narcotine with reagents, 332
- nicotine with reagents, 328
- nitric acid with metals, 267
  - with reagents, 203
- oxalic acid with reagents, 187
- phosphomaunite with reagents, 297
- phosphoric acid with reagents, 182
- pyrophosphoric acid with reagents, 185
- quinine with reagents, 334
- salts of volatile inorganic acids with sulphuric acid, 214
- second basic group with special reagents, 49
- silicic acids with reagents, 188
- sixth basic group with special reagents, 138
- starch with reagents, 323
- strychnine with reagents, 336
- succinic acid with reagents, 222
- sugar of milk with reagents, 295
- sulphuric acid with reagents, 178
- sulphurous acid with reagents, 179
- tannic acid with reagents, 223
- tartaric acid with reagents, 217
- taurocholic acid with reagents, 305
- taurocholalic acid with reagents, 305
- thiosulphuric acid with reagents, 180
- third basic group with special reagents, 62
- titanic oxide with reagents, 97
- uratic oxide with reagents, 97
- urea with reagents, 298
- uric acid with reagents, 227
- xanthine with reagents, 306
- Benzamidacetic acid, behavior of, with reagents, 303
  - composition of, 303
  - properties of, 303
- Benzoic acid, behavior of, with reagents, 222
  - detection of, 230
- Bile acids, examination for, 312
  - coloring matter, examination for, 312
  - coloring matter of, 307
  - in urine, 315
  - Pettenkofer's test for, 304, 309
  - properties of, 308
  - tests for, 309
- Bilirubine, behavior of, with reagents, 307
  - composition of, 307
  - detection of, 307
  - properties of, 307
- Biliverdine, properties of, 308
- Bluoxide of lead, 157
- Bismuth compounds, blowpipe test for, 152
  - characteristic tests, 153
  - flame reactions, 152
  - properties of, 152
- Bismuthic anhydride, 152
- dioxide, 153
- Bismuthous chloride, properties of, 145
  - nitrate, properties of, 146
  - oxide, properties of, 143

## Bismuthous—

- salts, properties of, 146
- sulphide, properties of, 144
- Bismuth, properties of, 142, 152
- Blood, coloring matter of, 308
  - tests for, 308
- Blowpipe, 351
  - operations, 237
    - supports for, 353
  - test for aluminic compounds, 85
  - antimony compounds, 118
  - argentic compounds, 143
  - bismuth compounds, 152
  - bromides, 200
  - chlorides, 195
  - chromic compounds, 85
  - cohalt compounds, 73
  - cupric compounds, 159
  - iodides, 197
  - lead, 156
  - manganese, 69
  - nickel compounds, 72
  - silicic acid, 191
  - sulphates, 179
  - tin compounds, 115
  - zincic compounds, 70
- Boracic acid, behavior of, with reagents, 180
  - characteristic tests for, 211
- Borax as reagent, 381
- Brazil-wood paper, 386
- Bromides, blowpipe test for, 200
- Bromine, detection of, in presence of iodine and chlorine, 199
- Brucine, behavior of, with reagents, 339
  - composition of, 339
  - properties of, 339
- Bunsen's flame reactions, 260
  - gas lamp, 358
- CADMIC chloride, properties of, 145
  - nitrate, properties of, 146
  - oxide, properties of, 143
  - salts, properties of, 146
  - sulphide, properties of, 144
- Cadmium and copper, separation of, 159
  - compounds, blowpipe tests for, 154
  - flame reactions, 154
  - properties of, 154
- Calcic carbonate in calculi, 319
  - chloride as reagent, 382
  - properties of, 53
  - compounds, characteristic tests for, 57
    - flame reactions, 56
    - properties of, 56
    - special tests for, 56
  - nitrate, properties of, 53
  - oxalate, detection of, 92
  - in calculi, 319
  - oxide, properties of, 53
  - phosphate, detection of, 91
  - in calculi, 319
  - salts, general character of, 54
  - sulphate as reagent, 382
  - properties of, 53
  - sulphite, properties of, 52
  - urate in calculi, 319
- Calcium, properties of, 51, 56
- Calculi, analysis of, 317

- Calculi**—  
 behavior of, on heating, 817  
 classification of, 817  
 composition of, 817  
 containing ammoniac urates, 318  
 cholesterol, 318  
 cystine, 318  
 fibrin, 318  
 uric acid, 318  
 xanthine, 318
- Cane-sugar**, behavior of, with reagents, 325  
 composition of, 325  
 properties of, 325
- Caramel**, 325
- Carbonates**, properties of, 186
- Carbonic acid**, behavior of, with reagents, 185  
 characteristic tests for, 211  
 precautions in examining for, 187
- Cassia**, behavior of, with reagents, 288  
 composition of, 280  
 detection of, 290  
 examination for, 310  
 properties of, 278, 288, 320
- Cellulose**, behavior of, with reagents, 321  
 composition of, 321  
 properties of, 321
- Characteristic reagents**, 26
- Tests for aluminic compounds**, 85  
 ammoniac compounds, 42  
 antimony compounds, 118  
 argentic compounds, 148  
 arsenic acid, 211  
 arsenious acid, 211  
 baric compounds, 55  
 bismuth compounds, 152  
 boracic acid, 211  
 calcic compounds, 57  
 carbonic acid, 211  
 chloric acid, 212  
 chromic acid, 211  
   compounds, 88  
 cobalt compounds, 74  
 cupric compounds, 159  
 ferric compounds, 87  
 ferrous compounds, 87  
 hydriodic acid, 212  
 hydrochloric acid, 212  
 hydrocyanic acid, 212  
 hydrofluoric acid, 211  
 hydrosulphuric acid, 212  
 lead compounds, 157  
 lithic compounds, 46  
 magnesian compounds, 59  
 manganese compounds, 70  
 mercury compounds, 152  
 nickel compounds, 72  
 nitric acid, 212  
 oxalic acid, 211  
 phosphoric acid, 211  
 potassic compounds, 44  
 silicic acid, 211  
 sodic compounds, 46  
 stannic compounds, 56  
 sulphuric acid, 211  
 uranium compounds, 97  
 zinc compounds, 70
- Chlorates**, properties of, 207
- Chloric acid**, behavior of, with reagents, 206  
 characteristic tests for, 212
- Chlorides**, blowpipe test for, 195
- Chlorine as reagent**, 378  
 detection of, 195
- Cholasperryhu**, behavior of, with reagents, 316  
 composition of, 307  
 detection of, 307  
 properties of, 307
- Cholestrin**, behavior of, with reagents, 307, 323  
 composition of, 307  
 in calculi, 316  
 properties of, 307
- Choudrin**, behavior of, with reagents, 293  
 composition of, 291  
 detection of, 291, 294  
 examination for, 311  
 oxidation of, 291  
 properties of, 291
- Chromates**, properties of, 176
- Chromic acid**, behavior of, with reagents, 176  
 characteristic tests for, 211  
 anhydride, properties of, 176  
 chloride, properties of, 52  
 compounds, blowpipe tests for, 85  
 characteristic tests for, 56  
 properties of, 84  
 special tests for, 86  
 oxide, properties of, 80  
 phosphates, properties of, 90  
 nitrate, properties of, 52  
 sulphate, properties of, 82  
 sulphide, properties of, 81
- Chromium**, properties of, 79, 85
- Cinchona**, behavior of, with reagents, 336  
 composition of, 336  
 properties of, 336
- Citrates**, properties of, 219
- Citric acid**, behavior of, with reagents, 219  
 detection of, 229  
 preparation of, 219
- Classification of acids**, 175  
 calculi, 817  
 inorganic acids, 208  
 organic acids, 228
- Coagulation of milk**, 288
- Cobalt compounds**, blowpipe tests for, 73  
 characteristic tests for, 74  
 flame reactions, 73  
 properties of, 72  
 special tests for, 72
- Cobaltic nitrate as reagent**, 383
- Cobaltous chloride**, properties of, 67  
 nitrate, properties of, 67  
 oxide, properties of, 65  
 salts, properties of, 68  
 sulphate, properties of, 67  
 sulphide, properties of, 66
- Cobalt**, 65, 72
- Coloration of flama**, 237
- Coloring matter of the bile**, 307  
 examination for, 212  
 in calculi, 319  
 blood, 308  
 urine, 307
- Composition of albumen**, 280  
 bilirubine, 307  
 brucine, 339  
 calculi, 317

Composition of—  
 cane-sugar, 325  
 casein, 280  
 cellulose, 321  
 cholepyrrhio, 307  
 cholestrin, 307  
 chondriu, 291  
 cinchouine, 336  
 creatio, 301  
 creatinine, 300  
 cystine, 305  
 fibrin, 280  
 gelatin, 292  
 glucose, 295  
 glyco-cholalic acid, 304  
 grape-sugar, 295  
 gum, 324  
 hippuric acid, 303  
 ioseite, 297  
 lactic acid, 302  
 lactin, 295  
 lactose, 295  
 lignin, 321  
 meconic acid, 340  
 milk-sugar, 295  
 morphine, 329  
 narcotine, 332  
 nicotine, 328  
 phaseomannite, 297  
 quinine, 334  
 silicates, 190  
 starch, 323  
 strychnine, 336  
 sugar of milk, 295  
 taurocholalic acid, 305  
 taurocholic acid, 305  
 urea, 295  
 urine, 314  
 xanthine, 306

Constituents of ash of organic substances, 274

Constitution of the albuminoids, Strecker's views, 282  
 Gerhardt's views, 281  
 Mulder's views, 281

Conversion of alcohol into acetic acid, 225

Copper and cadmium, separation of, 159  
 detection of, in organic liquids, 158  
 solids, 159  
 properties of, 142, 157  
 turnings as reagents, 354

Creatine, behavior of, with reagents, 301  
 composition of, 301  
 examination for, 313  
 properties of, 301

Creatinine, behavior of, with reagents, 300  
 composition of, 300  
 detection of, 301  
 examination for, 313  
 properties of, 301

Cupellation, 253

Cupric chloride, properties of, 145  
 compounds, blowpipe test for, 159  
 characteristic tests for, 159  
 flame reactions, 159  
 properties of, 153  
 nitrate, properties of, 146  
 oxide, properties of, 143  
 salts, properties of, 146  
 sulphate as reagent, 383  
 sulphide, properties of, 144

Cyetine, behavior of, with reagents, 305  
 composition of, 305  
 detection of, 306  
 in calculi, 318  
 properties of, 305

## DECANTATION, 349

Deflagration, 26, 351

Detection of acetic acid, 230  
 albumen, 290  
 antimony in organic mixtures, 117  
 arsenic by dialytic method, 126  
 by electrolysis, 129  
 in organic mixtures, 126

bezoic acid, 230  
 bilirubine, 307  
 bromine in presence of iodine and chlorine, 199  
 casein, 290  
 cholepyrrhin, 307  
 chondriu, 291, 294  
 citric acid, 229  
 copper in organic liquids, 158  
 solids, 159

creatinine, 301  
 cyetine, 306  
 fibrin, 290  
 formic acid, 230  
 free sulphuric acid in presence of a sulphate, 179  
 gallic acid, 230  
 gelatin, 292, 294  
 glucose, 295  
 grape-sugar, 296  
 hydrocyanic acid in mercuric cyanide, 202  
 organic mixtures, 202

iodates in presence of iodides, 197

lead in organic mixtures, 156  
 waters, 156

malic acid, 230

mercury in organic liquids, 150  
 solids, 151

opium in organic mixtures, 341

poisonous alkaloide in organic mixtures, 341  
 metals by electrolysis, 130

strychnine in organic mixtures, 338

succinic acid, 230  
 sugar, 297

taonic acid, 230  
 tartaric acid, 229  
 in presence of citric acid, 220

urea, 300  
 uric acid, 230  
 xanthine, 306

Determination of fusibility of solids, 255

Dialytic method for detection of arsenic, 126

Dibasic silicic acid, preparation of, 189

Dyhydric dipotassic metantimoniate as reagent, 381

Dieodic hydric phosphate, 380

Distillation, 350  
 of animal substances, 278

Distilled water, 385

## EFFERVESCENCE, 26

Electrolytic detection of arsenic, 128  
 of poisonous metals, 130

- Elements, behavior of, at high temperatures, 361  
     flame reactions of, 370  
 Emerald green, 114  
 Evaporation, 349  
 Examination for albumen, 310  
     ammonia, 35  
     bile acids, 312  
     casein, 311  
     chondrin, 311  
     coloring matter of the bile, 312  
     creatinine, 313  
     creatinine, 313  
     fatty matter, 313  
     globulin, 310  
     glucose, 312  
     haematin, 310  
     inorganic acids, 212, 234  
     lactic acid, 313  
     morphine, 332  
     mucus, 311  
     nicotine, 328  
     nitrogen, 270  
     organic acids, 230  
     phosphorus in organic substances, 272  
     potassic compounds, 35  
     pus, 310  
     sodic compounds, 35  
     sulphur in organic substances, 271  
     urea, 313  
     uric acid, 311  
 Examination of liquids, 233  
     solids, 236  
         with borax, 254  
         in closed tube, 241  
         in open tube, 247  
         on charcoal, 249  
         with cobaltic nitrate, 249  
         with sodic carbonate, 249  
 Exercises on first basic group, 46  
     second basic group, 59  
     third basic group, 74  
     fourth basic group, 88, 96  
     fifth basic group, 134  
     sixth basic group, 160  
     all basic groups, 174  
     inorganic acids, 215  
     organic acids, 232  
     organic alkaloids, 345  
     examination of liquids, 235  
         solids, 268  
     animal chemistry, 326  
 FATTY matter, examination for, 313  
     in urine, 316  
 Fermentation of glucose, 293  
     of grape-sugar, 296  
     test for sugar, 297  
 Ferments, 278  
 Ferric chloride as reagent, 382  
     properties of, 82  
     compounds, characteristic tests for, 87  
     nitrate, properties of, 82  
     oxide, properties of, 80  
     phosphate, properties of, 91  
     sulphate, properties of, 82  
     sulphide, properties of, 81  
 Ferrous chloride, properties of, 82  
     compounds, characteristic tests for, 87  
 Ferrons—  
     oxide, properties of, 80  
     sulphate as reagent, 382  
     properties of, 82  
     sulphide, 81  
 Fibrin, behavior of, with reagents, 287  
     composition of, 280  
     detection of, 290  
     in calculi, 318  
     properties of, 278, 286, 320  
 Fifth basic group, analysis of first method, 99  
     second method, 100  
     third method, 100  
     fourth method, 101  
     fifth method, 101  
     sixth method, 101  
     precautions in examining for, 171  
     precipitation of, 163  
 Films of volatile elements, 358, 367  
 Filtration, 348  
 First basic group, analysis of, 35  
     behavior of, with special reagents, 34  
     examination for, 168  
     precautions in analysis of, 36  
     properties of, 33  
 First group of inorganic acids, analysis of, 208  
     organic acids, analysis of, 228  
 Flame coloration, 237, 364  
     reactions, 260  
         of antimony compounds, 118  
         arsenic compounds, 131  
         baric compounds, 55  
         bismuth compounds, 152  
         cadmium compounds, 153  
         calcic compounds, 56  
         cobalt compounds, 73  
         cupric compounds, 159  
         iron compounds, 87  
         lead compounds, 156  
         lithic compounds, 46  
         mercury compounds, 151  
         nickel compounds, 72  
         potassic compounds, 35, 43  
         sodic compounds, 45  
         stroctic compounds, 56  
         tin compounds, 115  
         titanic compounds, 98  
         uranium compounds, 97  
         zincic compounds, 70  
         elements, 370  
 Formates, properties of, 226  
 Formation of precipitates, 26  
 Formic acid, behavior of, with reagents, 226  
     detection of, 230  
     preparation of, 226  
 Fourth basic group, analysis of first method, 77  
     second method, 77  
     third method, 79  
     behavior of, with special reagents, 78  
     precautions in analysis of, 92  
         in examining for, 172  
     precipitation of, 164  
 Fourth group of inorganic acids, analysis of, 210  
     organic acids, analysis of, 229  
 Fowler's solution, 114



- Fresenius's method of analysis of second basic group, 57  
 Fusibility of solids, determination of, 255  
 Fusible calculus, 319  
 Fusion, 350  
   of solids by deflagration, 264
- GALLIC ACID**, behavior of, with reagents, 224  
   detection of, 230  
   and tannic acids, separation of, 223  
 Gelatigenous substances, 291  
 Gelatine, behavior of, with reagents, 291  
   composition of, 291  
   detection of, 291, 294  
   oxidation of, 291  
   properties of, 291  
 General character of aluminic salts, 83  
   ammonic salts, 41  
   antimony salts, 112  
   argentic salts, 146  
   arsenic salts, 112  
   auric salts, 112  
   baric salts, 54  
   biemuthic salts, 146  
   cadmic salts, 146  
   calcic salts, 54  
   chromic salts, 83  
   cobaltous salts, 68  
   cupric salts, 146  
   ferric salts, 83  
   ferrous salts, 83  
   lithic salts, 41  
   magnesian salts, 54  
   manganous salts, 68  
   mercuric salts, 146  
   mercurous salts, 146  
   nickelous salts, 68  
   platinic salts, 112  
   plumbic salts, 146  
   potassic salts, 41  
   sodic salts, 41  
   stannic salts, 112  
   stannous salts, 112  
   strontic salts, 54  
   zincic salts, 68
- Gerhardt's views on the constitution of the albuminoids, 281  
 Globulin, examination for, 310  
   properties of, 289  
 Glucose, behavior of, with reagents, 294  
   composition of, 295  
   detection of, 296  
   examination for, 312  
   fermentation of, 296  
   properties of, 295  
 Gluten, properties of, 320  
 Glutin, behavior of, with reagents, 292  
 Glyco-cholalic acid, behavior of, with reagents, 304  
   composition of, 304  
   properties of, 304  
 Glycocholic acid, behavior of, with reagents, 304  
   composition of, 304  
   properties of, 304  
 Glyco-byochohic acid, behavior of, with reagents, 304  
   composition of, 304  
   properties of, 304  
 Gold, properties of, 102, 132  
   residues, treatment of, 359  
 Grape-sugar, behavior of, with reagents, 295
- Grape-sugar—  
   composition of, 295  
   detection of, 295  
   fermentation of, 296  
   properties of, 295  
 Group reagents, 26  
   behavior of basic groups with, 166  
 Gum, behavior of, with reagents, 324  
   composition of, 324  
   properties of, 324
- HÆMATIN**, examination for, 310  
   properties of, 308  
 Hippuric acid, behavior of, with reagents, 303  
   composition of, 303  
   properties of, 303  
 How the book ought to be studied, 27  
 Hydric peroxide, preparation of, 178  
 Hydride of antimony, properties of, 111  
   arsenic, properties of, 111  
 Hydriodic acid, behavior of, with reagents, 196  
   characteristic tests for, 212  
 Hydrobromic acid, behavior of, with reagents, 195  
 Hydrochloric acid as reagent, 373  
   behavior of, with reagents, 194  
   characteristic tests for, 212  
 Hydrocyanic acid, behavior of, with reagents, 200  
   characteristic tests for, 212  
   detection of, in mercuric cyanide, 202  
   in organic mixtures, 202  
   test-papers for, 336  
 Hydrofluosillicic acid as reagent, 376  
 Hydrofluoric acid, behavior of, with reagents, 191  
   characteristic tests for, 211  
 Hydrosulphuric acid as reagent, 375  
   behavior of, with reagents, 193  
   characteristic tests for, 212  
 Hyposulphurous acid, behavior of, with reagents, 180
- INDIGO**, solution of, as reagent, 355  
   ignition, 350  
 Imperfect precipitation, 29  
 Inorganic acids, classification of, 208  
   examination for, 212  
   first group of, analysis of, 208  
   second group of, analysis of, 208  
   third group of, analysis of, 208  
   fourth group of, analysis of, 210  
 Inosite, behavior of, with reagents, 297  
   composition of, 297  
   properties of, 297  
 Iodates, detection of, in presence of iodides, 198  
 Iodic acid, behavior of, with reagents, 197  
 Iodides, blowpipe test for, 197  
 Iodine, detection of, 196, 197  
 Iron compounds, flame reactions, 87  
   properties of, 86  
   special tests for, 86  
   liquor, 224  
   properties of, 79, 84
- LACTIC ACID**, behavior of, with reagents, 302  
   composition of, 302

- Lactic acid**—  
 examination for, 313  
 properties of, 302
- Lactin**, behavior of, with reagents, 295  
 composition of, 295  
 properties of, 295
- Lactose**, behavior of, with reagents, 295  
 composition of, 295  
 properties of, 295
- Lead**, action of water on, 154  
 binoxide, 154  
 compounds, blowpipe test for, 156  
 characteristic tests for, 157  
 flame reactions, 156  
 detection of, in organic mixtures, 156  
 waters, 156  
 properties of, 142, 154  
 suboxide, 157
- Legamine**, properties of, 320
- Lignin**, behavior of, with reagents, 321  
 composition of, 321  
 properties of, 321
- Lime-water** as reagent, 382
- List of apparatus**, 386
- Litharge**, 154
- Lithic chloride**, properties of, 40  
 compounds, characteristic tests for, 46  
 flame reactions, 46  
 properties of, 46  
 special tests for, 46  
 hydrate, preparation of, 37  
 oxide, properties of, 33, 37
- Lithium**, properties of, 37
- Litmus paper**, preparation of, 335
- MAGNESIC ammonic phosphate** in cal-  
 coh, 319  
 chloride, properties of, 53  
 compounds, characteristic tests for, 59  
 properties of, 58  
 special tests for, 58  
 nitrate, properties of, 53  
 oxide, properties of, 51  
 salts, general character of, 54  
 sulphate as reagent, 382  
 properties of, 53  
 sulphide, properties of, 52  
 urate in caluli, 319
- Magnesium**, properties of, 51, 58
- Malates**, properties of, 221
- Malic acid**, behavior of, with reagents, 221  
 detection of, 230
- Manganese**, blowpipe test for, 69  
 compounds, characteristic tests for,  
 70  
 properties of, 69  
 special tests for, 69  
 properties of, 65, 69
- Manganous chloride**, properties of, 67  
 nitrate, properties of, 67  
 oxide, properties of, 65  
 salts, properties of, 68  
 sulphate, properties of, 67  
 sulphide, properties of, 66
- Marsh's test** for arsenic, 122  
 precautions, 124
- Massicot**, 154
- Meeonite acid**, behavior of, with reagents,  
 340  
 composition of, 340  
 properties of, 310
- Melaanic acid**, 296
- Melting point** of substances, 364
- Mercuric chloride** as reagent, 383  
 properties of, 145  
 nitrate, properties of, 146  
 oxide, properties of, 143  
 salts, properties of, 146  
 sulphide, properties of, 144
- Mercurous chloride**, properties of, 145  
 nitrate as reagent, 382  
 properties of, 146  
 oxide, properties of, 143  
 salts, properties of, 146  
 sulphate, properties of, 146  
 sulphide, properties of, 144
- Mercury compounds**, characteristic tests  
 for, 152  
 flame reactions, 151  
 properties of, 148  
 special tests for, 150  
 detection of, in organic liquids, 150  
 solids, 151  
 properties of, 142, 148
- Metalbumin**, 286
- Metals of first basic group**, 37
- Metaphosphoric acid**, behavior of, with  
 reagents, 185
- Metastannic hydrate**, properties of, 113
- Microcosmic salt** as reagent, 381
- Milk**, coagulation of, 289
- Milk-sugar**, behavior of, with reagents,  
 295  
 composition of, 295  
 properties of, 295
- Morphine**, behavior of, with reagents, 329  
 composition of, 329  
 examination for, 332  
 properties of, 329
- Mucns**, examination for, 311
- Mulder's views** on the constitution of the  
 aluminoids, 281
- NARCOTINE**, behavior of, with re-  
 agents, 332  
 composition of, 332  
 examination for, 328  
 properties of, 332
- Nessler's test** for ammonia, 42  
 preparation of, 354
- Nickel compounds**, blowpipe test for, 72  
 characteristic tests for, 72  
 flame reactions, 72  
 properties of, 71  
 properties of, 65, 71
- Nickelous chloride**, properties of, 67  
 nitrate, properties of, 67  
 oxide, properties of, 65  
 salts, properties of, 68  
 sulphate, properties of, 67  
 sulphide, properties of, 66
- Nicotine**, behavior of, with reagents, 328  
 composition of, 328  
 properties of, 328
- Nitrates of first basic group**, 37  
 properties of, 203, 206
- Nitric acid** as reagent, 373  
 behavior of, with metals, 267  
 reagents, 203  
 characteristic tests for, 212
- Nitrogen**, examination for, 270
- Nitro-hydrochloric acid** as reagent, 373

**OPIUM**, detection of, in organic mixtures, 341

**Organic acids**, 216

classification of, 228

preliminary examination for, 231

examination for, 230

analysis of first group of, 228

second group of, 229

third group of, 229

fourth group of, 229

**Organic substances**, analysis of ash of, 273

constituents of ash of, 274

analysis of, 269

proximate analysis of, 272

**Oxalates**, properties of, 92, 187

**Oxalic acid** as reagent, 376

behavior of, with reagents, 187

characteristic tests for, 211

**Oxidation** of animal substances, 278

chondrin, 291

gelatin, 291

substances, 365

**Oxides** of first basic group, 37

**PARALBUMIN**, 286

Pettenkofer's test for bile, 304, 309

**Phascomannite**, behavior of, with reagents, 297

composition of, 297

properties of, 297

**Phenomena** accompanying chemical change, 26

**Phosphates**, properties of, 90, 182

**Phosphoric acid**, behavior of, with reagents, 182

characteristic tests for, 211

separation of, from alkaline earths, 183

anhydride, preparation of, 182

**Phosphorus**, detection of, 184

examination for, in organic substances, 272

**Photo-chemical method** of analysis of second basic group, 58

**Photo-chemistry**, 370

**Platinic chloride** as reagent, 383

properties of, 110

compounds, properties of, 133

special tests for, 133

oxide, properties of, 104

salts, properties of, 114

sulphide, properties of, 105

**Platinous oxide**, 134

**Platinum**, properties of, 102, 133

residues, treatment of, 388

**Plumbic acetate** as reagent, 382

chloride, properties of, 145

compounds, properties of, 154

nitrate, properties of, 146

oxide, properties of, 143

peroxide as reagent, 384

salts, properties of, 146

sulphate, properties of, 146

sulphide, properties of, 144

**Poisonous metals**, detection of, by electrolysis, 130

**Polysulphides**, properties of, 40, 193

**Potassic antimonious tartrate**, preparation of, 114

**Potassic**—

arsenite, 114

chloride, properties of, 40

chromate, as reagent, 379

compounds, characteristic tests for, 44

examination for, 35

flame reactions, 43

properties of, 42

special tests for, 42

cyanide as reagent, 379

ferricyanide as reagent, 378

ferrocyanide as reagent, 378

hydrate, preparation of, 37

nitrate, properties of, 40

nitrite as reagent, 378

oxide, properties of, 37

sulphate as reagent, 378

properties of, 40

sulphide, preparation of, 39

urate in calculi, 319

**Potassium**, properties of, 37, 42

**Precautions** in analysis of first basic group, 36

second basic group, 51

third basic group, 64

fourth basic group, 92

fifth basic group, 171

sixth basic group, 140

in examining for carbonic acid, 187

first basic group, 36

second basic group, 174

third basic group, 173

fourth basic group, 172

fifth basic group, 171

sixth basic group, 169

**Precipitation**, 347

of second basic group, 168

third basic group, 165

fourth basic group, 164

fifth basic group, 163

sixth basic group, 163

**Preliminary examination** for organic acids, 231

**Preparation** of blue litmus paper, 385

reddened litmus paper, 385

Nessler's test for ammonia, 384

turmeric paper, 386

**Protein** substances, 278

**Protein**, 281

**Proximate analysis** of animal substances, 277

organic substances, 272

**Pus**, examination for, 311

**Pyroligneous acid**, 225

**Pyrophosphoric acid**, behavior of, with reagents, 185

**Properties** of albumen, 279, 282, 320

bile, 309

bilirubine, 307

biliverdine, 308

brucine, 339

cane-sugar, 325

casein, 278, 288, 320

cellulose, 321

cholleypyrrhin, 307

cholestrin, 307

chondrin, 291

cinchonine, 336

creatin, 301

creatinine, 300

cystine, 305

## Properties of—

fibrin, 278, 286, 320  
 gelatin, 291  
 globulin, 289  
 glucose, 295  
 gluten, 320  
 glycocholic acid, 304  
 grape-sugar, 295  
 gum, 324  
 hæmatin, 308  
 hippuric acid, 302  
 inositol, 297  
 lactic acid, 302  
 legumine, 320  
 lignin, 321  
 meconic acid, 340  
 milk-sugar, 294  
 morphine, 329  
 narcotine, 332  
 nicotine, 328  
 phaseomannite, 297  
 quinine, 334  
 starch, 323  
 strychnine, 336  
 sugar of milk, 295  
 taurocholic acid, 305  
 taurocholic acid, 305  
 urea, 298  
 vitellin, 290  
 xanthine, 306

**Q**UININE, behavior of, with reagents, 334  
 composition of, 334  
 properties of, 334  
 test for, 335

**R**EACTIONS, 26

Reagent papers, 385

Reagents, 26  
 characteristic, 26  
 group, 26  
 special, 26

Red lead, 167  
 liquor, 224

Reduction of substances, 365

Reisach's test for arsenic, 125

Residues, treatment of, 387

**S**ARCOLACTIC ACID, properties of, 302

Scheele's green, 114

Schweinfurt green, 114

Second basic group, analysis of, 47  
 behavior of, with special reagents, 49

Presenue's method of analysis of, 57

precautions in analysis of, 51  
 photo-chemical method of analysis of, 57

precautions in examining for, 174  
 precipitation of, 168

group of inorganic acids, analysis of, 208

organic acids, analysis of, 229

Sediments in urine, 316

Separation of copper and cadmium, 150  
 phosphoric acids from the alkaline earths, 183

tanalic and gallic acids, 223

Silicates, composition of, 190

Silicic acid, behavior of, with reagents, 188

blowpipe test for, 191  
 characteristic tests for, 211  
 dibasic, preparation of, 189

anhydride, properties of, 189

Silver, properties of, 142, 147

residues, treatment of, 387

salts, colors of, 209

Sixth basic group, analysis of, 136

precautions, 140

precautions in examining for, 169

precipitation of, 163

exercises on, 160

Sodic ammonio hydric phosphate as reagent, 381

and potassic carbonate as reagent, 381

acetate, 380

carbonate, 380

chloride, properties of, 40

compounds, characteristic tests for, 46

examination for, 35

flame reactions, 44

properties of, 44

special tests for, 45

hydrate as reagent, 380

preparation of, 37

hydric sulphite as reagent, 380

tartrate as reagent, 375

nitrate, properties of, 40

oxide, properties of, 37

sulphate, properties of, 40

sulphide, preparation of, 39

urate in calculi, 319

Sodium, properties of, 37

Solids, determination of solubility of, 255

insoluble in acids, analysis of, 262

soluble in acids, analysis of, 261

in water, analysis of, 261

Solution, 346

of indigo as reagent, 385

Sources of error, 29

Special reagents, 26

tests for ammoniac compounds, 42

antimony compounds, 117

arsenic compounds, 132

baric compounds, 55

calcic compounds, 56

chromic compounds, 55

cobalt compounds, 72

iron compounds, 56

lithic compounds, 46

magnesian compounds, 58

manganous compounds, 69

potassic compounds, 42

sodic compounds, 45

strontic compounds, 56

tin compounds, 115

zinc compounds, 70

Stannic chloride, properties of, 103

hydrate, properties of, 113

oxide, properties of, 104

salts, properties of, 114

sulphide, properties of, 105

Stannous chloride as reagent, 384

properties of, 108

oxide, properties of, 104

salts, properties of, 110, 114

sulphide, properties of, 105

Starch, behavior of, with reagents, 323

- Starch—  
 composition of, 323  
 properties of, 323  
 Strecker's views on the constitution of the albuminoids, 282  
 Strontic chloride, properties of, 53  
 compounds, characteristic tests for, 55  
 flame reactions, 56  
 properties of, 56  
 special tests for, 56  
 nitrate, properties of, 53  
 oxido, properties of, 51  
 salts, general characters of, 54  
 sulphate, properties of, 53  
 sulphide, properties of, 52  
 Strontium, properties of, 51, 55  
 Strychnine, behavior of, with reagents, 337  
 composition of, 337  
 detection of, 338  
 properties of, 337  
 Sublimation, 350  
 Suboxide of lead, 157  
 Succinates, properties of, 223  
 Succinic acid, behavior of, with reagents, 222  
 detection of, 230  
 Sugar, detection of, 296  
 fermentation test for, 297  
 in urine, 315  
 of milk, behavior of, with reagents, 295  
 composition of, 295  
 properties of, 295  
 Trommer's test for, 296  
 Sulphates, blowpipe test for, 179  
 of first basic group, 37  
 properties of, 178  
 Sulph-hydrates, properties of, 39, 52, 193  
 Sulphides of first basic group, 37  
 properties of, 193  
 Sulphur, detection of, 194  
 examination for, in organic substances, 271  
 Sulphuric acid as reagent, 374  
 behavior of, with reagents, 178  
 characteristic tests for, 211  
 detection of, in presence of a sulphate, 179  
 anhydride, properties of, 178  
 Sulphurous acid, behavior of, with reagents, 179  
 properties of, 179  
 anhydride as reagent, 376  
 Sulphur salts, formation of, 106  
 Supports for blowpipe operations, 353
- TANNIC ACID**, behavior of, with reagents, 223  
 detection of, 230  
 and gallic acids, separation of, 224  
 Tartar emetic, preparation of, 113  
 Tartaric acid as reagent, 375  
 behavior of, with reagents, 217  
 detection of, 229  
 in presence of citric acid, 220  
 preparation of, 217  
 Tartrates, properties of, 217
- Taurocholalic acid, behavior of, with reagents, 305  
 composition of, 305  
 properties of, 305  
 Taurocholic acid, behavior of, with reagents, 305  
 composition of, 305  
 properties of, 305  
 Tests, 26  
 for bile, 309  
 for blood, 308  
 for quinine, 335  
 Test-papers for hydrocyanic acid, 386  
 Third basic group, analysis of, 61  
 behavior of, with special reagents, 62  
 precautions in analysis of, 64  
 in examining for, 173  
 precipitation of, 165  
 group of inorganic acids, analysis of, 209  
 organic acids, analysis of, 229  
 Thiosulphuric acid, behavior of, with reagents, 180  
 Tin compounds, blowpipe test for, 115  
 flame reactions, 116  
 properties of, 115  
 special tests for, 115  
 properties of, 102, 115  
 Titanic compounds, flame reactions, 98  
 oxide, behavior of, with reagents, 97  
 properties of, 97  
 Treatment of gold residues, 389  
 platinum residues, 388  
 silver residues, 387  
 Trommer's test for sugar, 297  
 Turmeric paper, preparation of, 386  
 Type metal, composition of, 117
- URANIC OXIDE**, behavior of, with reagents, 97  
 properties of, 97  
 Uranium compounds, characteristic tests for, 97  
 flame reactions, 97  
 Urates, properties of, 227  
 Urea, behavior of, with reagents, 298  
 composition of, 298  
 detection of, 300  
 examination for, 313  
 properties of, 298  
 Uric acid, behavior of, with reagents, 227  
 detection of, 231  
 examination for, 311  
 Uric acid in calculi, 318  
 Urinary sediments, 316  
 Urine, analysis of, 277, 313  
 coloring matter of, 307  
 composition of, 313  
 containing bile, 315  
 fatty matters, 316  
 sugar, 315  
 Urochrome, 307
- VARIETIES** of albumen, 285  
 Vitellin, properties of, 290  
 Volatile elements which can be reduced as films, 358  
 Volatility of substances, 364

**W**ATER, action of, on lead, 154  
Waters, detection of lead in, 156  
Water, distilled, 385

**X**ANTHINE, behavior of with re-  
agents, 306  
composition of, 306  
detection of, 306  
in calenil, 318  
properties of, 306

**Z**INC as reagent, 384  
properties of, 65, 70  
Zinc chloride, properties of, 67  
compounds, blowpipe tests for, 70  
characteristic tests for, 71  
flame reactions, 70  
properties of, 71  
special tests for, 71  
nitrate, properties of, 67  
oxide, properties of, 65  
salts, properties of, 68  
sulphate, properties of, 67  
sulphite, properties of, 66







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